VI.—A *Chemical Study of the Phosphoric Acid and Potash Contents of the Wheat Soils of Broadbalk Field, Rothamsted.*

By BERNARD DYER, *D.Sc., F.I.C.*

Communicated by SIR J. HENRY GILBERT, *F.R.S.*

Received November 9,—Read November 15, 1900.

CONTENTS.

Introduction.

In 1894 the author contributed to the 'Journal of the Chemical Society' (vol. 65, 'Trans.,' March, 1894) a paper on "The Determination of Available Mineral Plant Food in Soils," in which the use of a 1 per cent. solution of citric acid was proposed as a means of approximately differentiating by means of chemical analysis between the total and the probably available phosphoric acid and potash in soils. The reasons leading up to the tentative adoption of this solution, together with a summary of previous literature on the subject, are given in the original paper, and it need, therefore, now only be said that the method was the result of an attempt to imitate, in the solvent used, the acidity of root-sap, based on a preliminary examination of the root acidity of 100 specimens of flowering plants representing some 20 natural orders.

In order to test the proposed method it was applied to 22 samples of soil drawn from the various plots in Hoos Field, Rothamsted, on which barley under very various manurial conditions had been continuously grown for over forty years. The samples were placed at the author's disposal by the kindness of Sir John Lawes and Sir Henry Gilbert. The results of this investigation, which are fully set forth in the paper referred to, were of sufficient interest to lead to the undertaking of a similar but much more extended examination of the soils of the Rothamsted wheat plots in Broadbalk Field.

These plots have been continuously under wheat now for considerably more than fifty years. The manurial history of each plot and its yearly yield of grain and straw are all on record, and periodical analyses of the ashes of each year's crop from most of the plots have been completed sufficiently to allow of an estimate of the yearly removal of both phosphoric acid and potash. Furthermore, the soil of each plot was sampled in 1865 and in 1881, as well as in 1893, the three sets of samples

representing not only the surface soil (first 9 inches), but also the second and third depths, each to the extent of 9 inches.

Sir JOHN LAWES and Sir HENRY GILBERT (on behalf of the LAWES' Agricultural Trust Committee) kindly placed these valuable samples at the author's disposal for the determination of the total phosphoric acid and of the potash soluble in strong mineral acid, but more particularly for the further investigation of the citric acid process by ascertaining the proportions of these constituents existing in the various soils at various periods of their history and at various depths, in such a condition as to yield themselves to this weak solvent.   It was considered that a correlation of such results with the accurately known history of the plots, on both debit and credit side, for so many years, could scarcely fail to be of scientific interest, and might be of practical value.

The results of this work are now recorded.

Summarised History of the Wheat Plots.

It will be convenient to give in the first place a tabular summary of the history of each of the plots represented by the samples referred to, including the average yield per acre of wheat and straw for the forty-two years ending in 1893, and also for the six years ending in 1894, and the estimated quantities of phosphoric acid and potash per acre added in manure and removed in crops during fifty years, viz., from 1844 to 1893 (see p. 238).

General Observations as to Soil and Subsoil Irregularities and Difficulties incidental to Representative Sampling.

The data in this table suggest many directions in which the examination of the mineral contents of the various soils at various depths might be expected to yield interesting results, and in the main such expectation has not been disappointed.   It is true that there are occasional anomalies or discrepancies, but this is not altogether remarkable, for in the first case it is obviously difficult, despite the care taken at Rothamsted in the task of periodical soil sampling, to obtain soil samples really representative, not in a merely qualitative, but in an accurately quantitative sense, of the plots from which they are drawn.

The plots, as a rule, are half an acre in extent, being subdivided into two " lands " —each of which, however, in certain cases, is treated as a separate plot.

The 1893 samples examined were averages of four samples from each plot, two being taken from each half or " land "—except in the cases of the " single land " plots, viz., 3, 4, 10A, and 10B, on each of which three samples were drawn, and of the " single land " plots 2A and 2B, on each of which four samples were drawn.   The area of soil taken in each separate sampling is 1 square foot for the first 9 inches, and a

Plot.	Annual manuring for 50 years (except for minor variations indicated on some of the plots prior to 1852).	Broadbalk wheat plots.				Phosphoric acid.		Potash.	
		Average yield per acre for 42 years (1852–93).		Average yield per acre for 6 years (1889–94).		Estimated addition in manures during 50 years.	* Estimated removal in crops during 50 years.	Estimated addition in manures during 50 years.	* Estimated removal in crops during 50 years.
		Wheat. bush.	Straw. cwt.	Wheat. bush.	Straw. cwt.	lb.	lb.	lb.	lb.
3	Unmanured continuously . .	$12\frac{3}{4}$	$10\frac{5}{8}$	$12\frac{3}{4}$	$9\frac{1}{8}$	0	467	0	761
4	Unmanured continuously since 1852 (previously superphosphate and ammonium salts)	$13\frac{1}{2}$	$10\frac{7}{8}$	$13\frac{1}{5}$	$9\frac{1}{5}$	506	528	235	848
10A	Ammonium salts, alone, 400 lb. yearly since 1844 (mineral manure in 1844)	$19\frac{1}{2}$	$17\frac{3}{4}$	$16\frac{1}{2}$	$13\frac{1}{2}$	82	582	74	1090
10B	Ammonium salts, alone, 400 lb. yearly since 1844 (except in 1846 and 1850; mineral manure in 1844, 1848, and 1850)	$21\frac{7}{8}$	20	18	$15\frac{1}{4}$	210	650	374	1205
7	Ammonium salts, 400 lb. Superphosphate, 3½ cwt. Potassium sulphate, 200 lb. (300 lb. up to 1858) Sodium sulphate, 100 lb. (200 lb. up to 1858.) Magnesium sulphate, 100 lb.	$32\frac{3}{4}$	$32\frac{3}{4}$	$34\frac{3}{4}$	$33\frac{5}{8}$	3107	1122	5037	2550
13	Ammonium salts, 400 lb. Superphosphate, 3½ cwt. Potassium sulphate, 200 lb. (300 lb. up to 1858.) (No sodium or magnesium salts.)	$31\frac{1}{4}$	$31\frac{1}{8}$	$32\frac{3}{8}$	$31\frac{3}{4}$	3181	1061	5287	2410
14	Ammonium salts, 400 lb. Superphosphate, 3½ cwt. Magnesium sulphate, 280 lb. (420 lb. up to 1858.) (No sodium or potassium salts since 1850.)	$30\frac{3}{4}$	$29\frac{3}{8}$	$29\frac{1}{4}$	$27\frac{1}{8}$	3216	1016	566†	1833
12	Ammonium salts, 400 lb. Superphosphate, 3½ cwt. Sodium sulphate, 366¼ lb. (550 lb up to 1858.) (No potassium or magnesium salts since 1851.)	$30\frac{1}{8}$	$28\frac{1}{2}$	$29\frac{1}{8}$	$25\frac{5}{8}$	3189	1005	588†	1743
11	Ammonium salts, 400 lb. Superphosphate, 3½ cwt. (No potassium, sodium, or magnesium salts.)	$24\frac{1}{2}$	23	$21\frac{3}{5}$	$20\frac{1}{2}$	3153	861	15†	1190
5	Superphosphate and potassium, sodium and magnesium sulphates, as on 7, but no nitrogen	$14\frac{3}{4}$	$12\frac{1}{4}$	$14\frac{3}{4}$	$10\frac{1}{2}$	3256	674	5203	1136
2B	14 tons farmyard manure (1843–44, and every year since)	$34\frac{5}{8}$	$32\frac{1}{4}$	$40\frac{7}{8}$	$38\frac{3}{4}$	3920	1301	11760	2478
2A	14 tons farmyard manure (commencing in 1884–85) .	—	—	$30\frac{1}{4}$	$28\frac{3}{8}$	—	—	—	—

* Estimated from analyses of separate samples of each year's grain and straw from each plot.   † Applied prior to 1852.

quarter of a square foot for the second and third 9 inches. The actual area represented by the samples is therefore in most cases less than $\frac{1}{5000}$ of the actual area of the plot represented, in the case of the first 9 inches or surface soil, and less than $\frac{1}{20000}$ of the area represented in the case of the second and third 9 inches.

In the case of single land plots already mentioned the fractions are larger, rising in the case of 2A and 2B to nearly $\frac{1}{3000}$ of the area of the plot in the case of the surface soil, and to about $\frac{1}{13000}$ in the case of the second and third depths.

The Rothamsted soil contains a considerable proportion of stones. The first 9 inches of soil in Broadbalk field contains on the average something like 14 per cent. of stones, removable by a $\frac{1}{4}$-inch sieve, the second 9 inches something like 12 per cent., and the third depth something like 7 per cent.

The most careful sampling cannot be relied on to ensure an accurate representation of both stones and fine soil in each sample, and it is therefore found necessary to eliminate the stones and estimate, from the average weighings of the various samples, the weight of fine soil per acre. Much minute care has been spent by Sir JOHN LAWES and Sir HENRY GILBERT in forming these estimates of acreage weights of fine soil in the various depths, and the estimates are probably on the average as substantially fair as it has been possible to make them. But it is obvious that when the contents of an acre of soil have to be calculated from the analyses of samples, the error in the estimated weight of fine soil per acre for any individual plot may well affect the calculation. Then, apart from the probability that no sample is entirely representative of the plots from which it is drawn, it is not easy to deal with the actual samples, consisting as they do of a mixture of clay, fine and coarse sand, and gravel, so accurately as to ensure that the small portion ultimately analysed shall quite fairly represent the bulk sample; while, even beyond this difficulty, we have to face the fact that even the best analytical manipulation involves some experimental error. When 10 grammes of soil are used for a determination, say, of phosphoric acid, and the quantity found is calculated out to lbs. per acre in a depth of 9 inches, the actual error of experiment has to be multiplied by some such figure as 120,000,000. Thus a difference of ·001 gramme (or ·01 per cent.) represents, in round numbers, 260 lb. per acre in 9 inches of soil; and even ·0001 gramme, working on 10 grammes of soil (or ·001 per cent.) affects an acreage estimate in 9 inches of soil to the extent of 26 lb. Of course the multiplication of error is less in those cases in which larger quantities of soil can be used. But at the best, the chances of error incidental to sampling, to analysis, and to acreage computation of the results, are sufficient to explain some of the anomalies that will be met with.

For example, when the various samples drawn from some of the individual plots at three different periods (1865, 1881, and 1893) are compared, allowing for the influences of intermediate cropping and manuring, differences will be found which are only to be explained on the ground that one or other of the set of samples could not have been satisfactorily representative, in a " mineral " sense at any rate, of its plot, showing

that the plot itself is not minerally uniform.   Seeing how difficult it is to find complete uniformity in the soil of any field, even within half an acre, this is not remarkable.

It must furthermore be noted here that the 1865 and 1881 samples from the chemically manured plots consisting of two "lands" were drawn from one "land" or half plot only, the two halves being in former years kept distinct owing to certain minor differences of manurial treatment in their earlier history.   Now, however, the two lands have in most cases ceased to be regarded as separate plots, and it was considered better in 1893 to draw the samples from both halves or lands ; but as the 1865 and 1881 samples examined represented only one land they are not quite strictly comparable with the 1893 samples, except in the case of the single land plots 10A and B and 2B. This, no doubt, may in itself account, in view of what has been already said, for some of the irregularities observed in comparing samples of the different years.

As would be expected, the lack of uniformity of composition is indicated less in the surface soils than in the subsoils.   The surface soil is subjected to the mixing operations of the plough, the harrow, and the hoe, and though these implements do not effect any considerable transference of soil from one end of a plot to another, and so do away with original differences of composition of spots remote from one another within the plot area, they nevertheless, continued for fifty odd years, must effect such a gradual mixing up of the surface soil as to render it every year less likely that a sample drawn from any arbitrarily chosen spot should differ very much from one drawn at any neighbouring spot on the same plot.

With the second and third depths it is otherwise.   No mixing of the subsoil goes on beyond that effected by worms or other natural agencies.   Furthermore, the excavations made in Broadbalk Field for the purpose of obtaining deep subsoil samples—for sampling is carried out to a considerably greater depth than that of the 27 inches of soil which form the subject of the present study—show that the subsoil both in its composition and in its depth as it gradually passes into the subjacent chalk is very variable.   For this reason, no doubt, some of the results obtained by the mineral analyses of the subsoil present anomalies which make it necessary to regard the results in a qualitative rather than in a quantitative sense.

Another point of difficulty is that, in comparing the composition of one plot with that of another, it is impossible, quite apart from local variations within each plot, to know how far the average surface soil of any one plot may have originally differed from that of all or any of its neighbours at the time of the commencement of the experiments.   For purposes of any attempt at quantitative comparisons it is necessary to implicitly assume some such original uniformity, thus introducing yet another possible source of error.   This too must be borne in mind in regarding the results of the attempts that have been made to compare a theoretical debtor and creditor account for the phosphoric acid of some of the plots with the quantity, condition, and distribution of the "assets" actually discovered by analysis.

Apart from natural or accidental inequalities of soil, it is scarcely necessary to point out in advance the many factors which might be expected to affect the distribution and condition of mineral plant food in soils so diversely manured as those with which we have to deal. It is not merely the quantity, nature, and condition of the manure materials added, and those of the elements removed by cropping, that are to be taken into account, but also the indirect effects of the liberal feeding or starvation of the crops as regards any one or more of the elements necessary to their growth. For upon this must largely depend their root development and the area in which they seek their food. The roots of wheat penetrate deeply, and no doubt they bring up from the lower subsoil plant food, of which some must be left to accumulate in their débris (roots and stubble) in the upper subsoil and surface soil. No doubt the general degree of luxuriance of any crop, and the plenitude or scarcity of any one or more constituents of food in the surface soil, connote some corresponding condition or habit of root growth which in the course of fifty years must affect not only the accumulation of root residuum, but also its relative distribution in the different layers of the soil. This consideration, however, while complicating the task of comparing soil with soil, adds to the interest to be derived from a patient study of the analytical results in connection with the field records.

General Bearing of the Results of the Investigation.

Before proceeding to a detailed account of the work it may be well to give briefly some idea of the general outcome of the results.

It will, then, be found that the differences between the quantities of total phosphoric acid existing in the soils of the different plots, unmanured and variously manured, correspond fairly well with the history of the plots; but that, as in the case of the barley soils, in the absence of a knowledge of such history, the differences in phosphoric acid percentage would not suffice to give any indication of the great differences in fertility really attributable to the phosphatic condition of the soils.

It will, however, be found that the relative proportions of phosphoric acid soluble in dilute citric acid solution do afford, on the whole, a striking index to the relative fertility of the soils as influenced by their phosphatic condition.

Even in the subsoils, in which the natural irregularities and variations of the soil are such that the total percentage of phosphoric acid lacks significance, the citric acid results will be frequently seen to show striking and consistent differences, and these will be found to be of interest when studied in connection with the problems of root range and subsoil feeding which will be hereafter discussed in examining the results of the individual plots.

With regard to potash, it will be seen that the percentage extracted from the soil by hydrochloric acid in the case of such soils as these—which contain a great abundance of potash in mineral combination—varies with the exact method of

extraction, and leads to results which are of very little utility, having regard to the purpose for which a soil analysis is ordinarily required.

The quantity of potash extracted by dilute citric acid solution, however, will be found, as in the case of phosphoric acid, to show variations which appear to be consistent in regard both to the actual fertility of the various soils and to the supply or non-supply of potash in the fertilisers used.

Where there has been a liberal supply of manurial phosphoric acid to the soil, in excess of the demands of the plants, it will be found that the greater proportion of the unconsumed phosphoric acid, though originally water-soluble, has accumulated in the surface or first 9 inches of the soil, though in the case of dung there is a very considerable descent into the two layers of subsoil examined, namely, the second and third depths of 9 inches.

Potassium, sodium, and magnesium salts will be seen to have exerted a distinct influence in the retention of the phosphoric acid in a less fixed and presumably more available condition than that in which we find it in the soils of the plots on which the use of superphosphate has not been accompanied by the application of these salts; and it will be also apparent that where these salts have been used in addition to superphosphate, without nitrogen (full supply of phosphoric acid and limited utilisation by the plant owing to lack of nitrogen), there is evidence that the salts have caused a very tangible descent of phosphoric acid into the second and even the third 9 inches.

The greatest accumulation of unused manurial potash, whether applied as dung or as potassium salts, is also found in the surface soil; but a large proportion is found in the citric-acid-soluble condition in the second and even the third 9 inches, especially in the dunged plots. In spite of the large surface accumulation, the examination of the subsoils by means of dilute citric acid solution appears to show that, even in a soil containing so much clay as that of Rothamsted, potash is far more migratory than phosphoric acid, and descends much lower into the subsoil.

The addition of sodium and magnesium sulphates to potassium sulphate, in presence of phosphates, seems to have exercised a distinct influence in retaining potash in a citric-acid-soluble and presumably available condition, the apparent tendency of a portion of the potash to pass into a stable form of combination with the soil being diminished.

It is also found that, even where no potassium salts are used, sodium and magnesium salts, in presence of phosphates and nitrogen, have exercised a marked influence in increasing the proportion of citric-acid-soluble potash, in the soil in all the depths examined. This accords well with the fact that, although no potassium salts have been applied to these plots for fifty years, their crops are larger, and contain a larger quantity of potash per acre than those grown on the plot manured with super-phosphate and ammonium salts alone.

The soils of certain of the plots which, for the greater part of the experimental

period, had been manured in exactly the same way, will be seen to show, when examined by the dilute citric acid method, differences which can be traced to variations in manurial treatment more than forty years previously.

With these prefatory observations we may proceed to consider the results, taking them in two separate sections, viz., those relating respectively to the phosphoric acid and to the potash contents of the soil.

Phosphoric Acid Results.

It will, perhaps, be most convenient at first to record the whole of the phosphoric acid figures, and subsequently to examine them in groups arranged according to the various points of view from which they appear to demand consideration.

The total phosphoric acid was in each case determined in 10 grammes of the dried soil by ignition and extraction with mineral acid. Duplicate determinations have in all cases been made, one with nitric acid only as a solvent, the other with hydrochloric acid—the chlorine being eliminated from the solution (after removal of the silica) by repeated evaporation with nitric acid. The phosphoric acid was in each case determined by Hehner's modification of the molybdic acid process, and in cases in which the duplicate determinations were not considered to be sufficiently close, further determinations were made to see which result was the more nearly accurate.

The citric acid results were obtained by treating a large quantity of soil (usually 200 grammes) with 1 per cent. citric acid solution, in the proportions of 1 litre of solvent to 100 grammes of soil, the soil being kept in the solution for seven days with frequent shaking. A quantity of solution representing 50 grammes of soil was taken for the determination of the phosphoric acid. The solution was evaporated to dryness, ignited, and the residue digested in strong hydrochloric acid,* the latter being subsequently expelled with nitric acid prior to determination of the phosphoric acid by the molybdic process. At least two determinations were made in every case. The following table shows the percentages of total phosphoric acid and citric-soluble phosphoric acid in all of the samples examined, and the same results calculated into weights per acre.

For these latter calculations the weights adopted for fine dry soil per acre were as follows :—

* Nitric acid must *not* be used for extraction ; nitric acid completely extracts the phosphoric acid from ignited *soil*, but fails to extract it from the ferruginous aluminous ash left on incineration of the citric acid extract.

1st 9 inches.

Lbs.

For Plots 3, 4, 5, 7, 10A, 10B, 11, 12, 13, and 14 in each year   2,592,621

„   Plot 2A, 1893   2,510,185

„   „   2B, 1865   2,478,780

„   „   2B, 1881   2,395,986

„   „   2B, 1893   2,333,891

2nd 9 inches.

For all plots in each year.   2,671,321

3rd 9 inches.

For all plots in each year.   2,791,501

SOILS FROM BROADBALK WHEAT FIELD, ROTHAMSTED.

Samples collected in 1865, 1881, and 1893.

Phosphoric Acid Determinations.

	Dissolved by strong hydrochloric or nitric acid.						Dissolved by 1 per cent. solution of citric acid.					
	1865.	1881.	1893.	1865.	1881.	1893.	1865.	1881.	1893.	1865.	1881.	1893.
	1st 9 inches of soil.											
Plot.	P_2O_5, per cent.			P_2O_5, lbs. per acre.			P_2O_5, per cent.			P_2O_5, lbs. per acre.		
3	·140	·131	·114	3630	3396	2956	·0094	·0074	·0078	244	192	202
4	—	—	·120	—	—	3111	—	—	·0100	—	—	259
10A	·146	·126	·123	3785	3267	3189	·0106	·0068	·0074	275	176	192
10B	—	·130	·126	—	3370	3267	—	·0092	·0074	—	239	192
7	—	—	·195	—	—	5056	—	—	·0547	—	—	1418
13	·174	·199	·205	4511	5159	5315	·0261	·0383	·0434	677	993	1125
14	·178	·189	·204	4615	4900	5289	·0257	·0364	·0442	666	944	1146
12	·183	·200	·201	4744	5185	5211	·0268	·0386	·0413	695	1001	1071
11	·177	·184	·197	4589	4770	5107	·0259	·0329	·0405	672	853	1050
5	—	—	·219	—	—	5678	—	—	·0642	—	—	1665
2A	—	—	·165	—	—	4142	—	—	·0321	—	—	806
2B	·189	·194	·215	4685	4648	5018	·035 5	·0372	·0560	880	891	1307

SOILS FROM BROADBALK WHEAT FIELD, ROTHAMSTED—*continued.*

	Dissolved by strong hydrochloric or nitric acid.						Dissolved by 1 per cent. solution of citric acid.					
	1865.	1881.	1893.	1865.	1881.	1893.	1865.	1881.	1893.	1865.	1881.	1893.
				2nd 9 inches of soil.								
Plot.	P_2O_5, per cent.			P_2O_5, lbs. per acre.			P_2O_5, per cent.			P_2O_5, lbs. per acre.		
3	·116	·093	·113	3099	2484	3019	·0029	·0020	·0041	78	53	110
4	—	—	·106	—	—	2832	—	—	·0024	—	—	64
10A	·128	·101	·111	3419	2698	2965	·0031	·0018	·0031	83	48	83
10B	—	·113	·123	—	3019	3286	—	·0028	·0043	—	75	115
7	—	—	·086	—	—	2297	—	—	·0038	—	—	102
13	·111	·108	·105	2965	2885	2805	·0022	·0019	·0027	59	51	72
14	·118	·105	·111	3152	2805	2965	·0024	·0016	·0023	64	43	61
12	·112	·112	·098	2992	2992	2618	·0019	·0020	·0035	51	53	94
11	·106	·107	·108	2832	2858	2885	·0022	·0017	·0028	59	45	75
5	—	—	·107	—	—	2858	—	—	·0052	—	—	139
2A	—	—	·095	—	—	2538	—	—	·0052	—	—	139
2B	·126	·111	·111	3366	2965	2965	·0044	·0031	·0094	118	83	251
				3rd 9 inches of soil.								
3	·092	·090	·097	2568	2512	2708	·0012	·0012	·0021	34	34	59
4	—	—	·097	—	—	2708	—	—	·0017	—	—	48
10A	·111	·090	·105	3099	2512	2931	·0014	·0013	·0018	39	36	50
10B	—	·104	·111	—	2903	3099	—	·0012	·0021	—	34	59
7	—	—	·074	—	—	2066	—	—	·0030	—	—	84
13	·093	·087	·081	2596	2429	2261	·0012	·0010	·0016	34	28	45
14	·121	·104	·113	3378	2903	3154	·0017	·0011	·0023	48	31	64
12	·103	·087	·082	2875	2429	2289	·0014	·0012	·0020	39	34	56
11	·098	·096	·091	2736	2680	2540	·0017	·0012	·0017	48	34	48
5	—	—	·112	—	—	3126	—	—	·0036	—	—	101
2A	—	—	·084	—	—	2345	—	—	·0028	—	—	78
2B	·103	·082	·083	2875	2289	2317	·0015	·0017	·0034	42	48	95

General Comparison of Plots Manured with Phosphates (or with Dung) and those not so Manured.

For the purpose of this comparison, which (outside of the special features of interest afforded by the relations of the various individual plots to each other) has a widely applicable interest as affecting the general question of the methods of soil analysis and of the interpretation of their results, it will be sufficient to consider the figures in a quasi-qualitative sense, having at the same time regard to the manurial history and crop yields of the plots ; and, for the moment, it will be most convenient to confine our attention to the 1893 samples of the surface soil or first 9 inches for it

is in this depth that the variations in phosphoric acid are mainly found, the greater part of the unused phosphates applied to a soil containing so much clay as the Rothamsted loams being evidently mainly retained in the surface soil, though, as we shall hereafter see, some portion does, under some conditions, find its way into the subsoil. But as long as we are merely regarding the figures from a general or qualitative point of view, and having in mind merely the bearing of analytical results on the question of the relative fertility of soils, we may very well, for the moment, neglect the lower depths.

The following table relating to the surface soil samples of 1893 shows the percentages of total and citric-soluble phosphoric acid in each separate plot, and the average yield of grain and straw for six recent years (1889 to 1894, the last named being the season following the soil sampling) :—

1893 Samples.

Plot.	Annual manuring for 50 years (with only minor variations during earlier years).	Percentage of phosporic acid (P₂O₅) in fine dry soil. 1st 9 inches.		Average yield per acre (1889–94).	
		Total.	Dissolved by 1 per cent. citric acid solution.	Wheat.	Straw.
3	Unmanured continuously	·114	·0078	bushel. $12\frac{3}{4}$	cwt. $9\frac{1}{8}$
4	„ „ since 1852	·120	·0100	$13\frac{1}{8}$	$9\frac{1}{8}$
10A	Ammonium salts only since 1844 .	·123	·0074	$16\frac{1}{2}$	$13\frac{1}{2}$
10B	„ „ „ 1850 .	·126	·0074	18	$15\frac{1}{4}$
7	Superphosphate and ammonium salts, with potassium, sodium and magnesium sulphates	·195	·0547	$34\frac{3}{4}$	$33\frac{5}{8}$
13	Superphosphate and ammonium salts, with potassium sulphate	·205	·0434	$32\frac{3}{8}$	$31\frac{3}{4}$
14	Superphosphate and ammonium salts, with magnesium sulphate	·204	·0442	$29\frac{1}{4}$	$27\frac{1}{8}$
12	Superphosphate and ammonium salts, with sodium sulphate	·201	·0413	$29\frac{1}{8}$	$25\frac{5}{8}$
11	Superphosphate and ammonium salts only	·197	·0405	$21\frac{3}{8}$	$20\frac{1}{2}$
5	Superphosphate and potassium, sodium and magnesium sulphates (no nitrogen)	·219	·0642	$14\frac{3}{4}$	$10\frac{1}{2}$
2B	14 tons farmyard manure	·215	·0560	$40\frac{7}{8}$	$38\frac{3}{4}$
2A	„ „ „ (commencing in 1884–5)	·165	·0321	$30\frac{1}{4}$	$28\frac{3}{8}$

These results may be condensed by averaging the four soils which have been wholly without phosphatic manure since 1850 ; and also the five soils continuously receiving superphosphate in conjunction with nitrogen.

1893 Samples.

Plots.	Annual manuring.	Percentage of phosphoric acid in fine dry soil (first 9 inches).		Average yield per acre, 1889–4.	
		Total.	Dissolved by 1 p. c. citric acid solution.	Wheat.	Straw.
3, 4, 10A, and 10B	No phosphates	·121	·0082	$15\frac{1}{8}$	$11\frac{3}{4}$
7, 13, 14, 12, 11	Superphosphate and ammonium salts, with and without alkaline salts	·200	·0448	$29\frac{3}{8}$	$27\frac{3}{4}$
5 . . .	Superphosphate and alkaline salts, without nitrogen	·219	·0642	$14\frac{3}{4}$	$10\frac{1}{2}$
2B . . .	14 tons farmyard manure for fifty years	·215	·0560	$40\frac{7}{8}$	$38\frac{3}{4}$
2A . . .	14 tons farmyard manure for nine years only	·165	·0321	$30\frac{1}{4}$	$28\frac{3}{8}$

We have thus reduced the plots to four classes. The first group is suffering from phosphatic starvation, aggravated, in two of the four plots comprising it, by a free supply of ammonium salts. The average yield has dropped to a little over 15 bushels of wheat per acre, and less than 12 cwt. of straw.

In the next group of five plots superphosphate has been freely and continuously supplied, as well as nitrogen in the form of ammonium salts ; while on four out of the five plots of this group " alkaline " salts (potassium, sodium, and magnesium salts, together or separately) have been likewise applied annually. Here the average yield of wheat is nearly double that of the former group, while the straw is more than two and a quarter times as great.

Then we have the plot which has received continuously an abundance of phosphatic and other mineral manure, but no nitrogen. Its yield is now poorer on the average than even the first group, for it is suffering from nitrogen starvation—shown even more strongly in the low straw yield than in the low yield of grain. The yield of both grain and straw, though less than the average yield of the first group, is, nevertheless, better than that of the unmanured plots 3 and 4 included in it, which are suffering from both nitrogen and mineral starvation. But its yield of grain is only half that of the group of soils supplied annually with nitrogen as well as minerals, and its yield of straw is not much more than one-third. Since it has received practically the same supply of phosphatic manure per acre as this group, we should (apart from the information derived from analyses of the crops) expect to find an additional accumulation of phosphates in this plot over and above that found in group 2.

Then we have the farmyard manure plots, the one dunged liberally for fifty years leading the way with a yield well above that of any of the other groups, both as regards grain and straw, and the other subjected to this liberal treatment for nine years only, but still, in virtue of its comparatively newly acquired fertility, giving a better yield than the average of the chemically-treated plots, though not so good a yield as the completely manured Plot 13.

The differences in phosphoric acid contents that one would be led to expect from the aforesaid considerations are qualitatively apparent in the figures for total phosphoric acid. Thus, the second group shows greatly more phosphoric acid than the first group. Again, on the other hand, it shows less than Plot 5. Intermediate is the long-dunged plot, while the plot more recently brought under dung treatment is intermediate between the 1st and 2nd group.

But these differences in *total* phosphoric acid, significant as they clearly are, in soils from the same field, would convey, apart from à *priori* knowledge of their origin and of their circumstances, no such information as to suggest the profound differences really existing in the phosphatic condition of the soils.

Average Ratio of Total Phosphoric Acid of Phosphated to that of Non-phosphated Soils.

To make this more clear the figures are best reduced to a simple proportion, taking the average quantity of phosphoric acid in the first group as unity. We then have :—

		Ratio of total phosphoric acid to that of plots receiving no phosphates.
Four plots	No phosphates	1·00 : 1
Five „	Phosphates and nitrogen, with and without alkaline salts , . . .	1·65 : 1
One plot	Phosphates and alkaline salts only	1·81 : 1
One „	Dung 50 years	1·78 : 1
One „	Dung 9 years	1·36 : 1

The four plots in the first group contain on the average over 3000 lbs. of phosphoric acid per acre in the first 9 inches of soil, to say nothing of further 6000 lbs. in the subjacent 18 inches. This is equivalent to nearly 3 tons of phosphate of lime per acre in the top soil, with 6 tons lying below, well within reach of the plant in its later stages of growth. In face of this enormous quantity of total phosphoric acid the wheat crop, which, under the most favourable circumstances, does not need more (and usually needs less) than some 30 lbs. of phosphoric acid per acre, is unable on these plots to do more than eke out a half-starved existence, even when nitrogen is freely supplied. The history of the crops clearly indicates that, of the total phosphates present in the soils of these plots, only a small proportion are in a form in which they

can be utilised.   Even in ordinary farming it is a familiar fact that, on soils con-
taining a good deal more phosphoric acid than this, a few cwts. of superphosphate
per acre will often make the difference between a full crop of roots and one that is all
but a failure.   This being so it is evident that such ratios as those just given for
total phosphoric acid would have little significance if we wished to compare soils from
different fields, or to judge of their relative mineral fertility, or to forecast the probable
advantage of applying phosphatic manure or the economy of withholding it.

Average Ratio of Citric-acid-soluble Phosphoric Acid of Phosphated to that of Non-phosphated Soils.

If, on the other hand, we take the phosphoric acid dissolved by a 1 per cent. solu-
tion of citric acid we find differences of an altogether different character; for, while
the ratios for total phosphoric acid between phosphatically manured and phosphati-
cally unmanured plots were all comprised within a ratio of 2 : 1, we find the citric
acid soluble ratios, as will be seen from the following table, to show approximately
such numbers as 4 : 1, 5 : 1, and nearly 8 : 1.

		Ratio of phosphoric acid soluble in 1 per cent. citric acid solution, to that of plots receiving no phosphates.
Four plots	No phosphates	1·00 : 1
Five „	Phosphates and nitrogen, with and without alkaline salts	5·46 : 1
One plot	Phosphates and alkaline salts only	7·83 : 1
One „	Dung 50 years	6·83 : 1
One „	Dung 9 years	3·91 : 1

Clearly the percentage of citric-acid-soluble phosphoric acid gives us overwhelm-
ingly clearer qualitative information as to the condition of the soils than any that
could be arrived at from a study of the mere total percentages, apart, as aforesaid,
from à priori topographical and historical knowledge.

Probable Limits of Phosphatic Deficiency and Sufficiency in Soils.

It will have been noticed that in only one case, on the phosphatically unmanured
plots, does the phosphoric acid soluble in citric acid reach ·01 per cent. of the surface
soil, the average number for these four plots being ·0082 per cent., corresponding to
a little over 200 lbs. per acre.   This figure corresponds almost exactly with the mean
figure obtained for the soils of the eight phosphatically starved barley plots from
Hoos Field during the investigation already referred to (see paper in 'Journal of the
Chemical Society,' 1894), as a result of which the author contented himself with
drawing the tentative conclusion that, when a soil is found by analysis to contain as

little as about ·01 per cent. of phosphoric acid soluble in a 1 per cent. solution of citric acid, used as described, it would be justifiable (as far as cereals are concerned) to assume that it stands in immediate need of phosphatic manure. That conclusion, therefore, appears to be well maintained by the new results obtained from the wheat soils. How far we may go in the other direction in venturing to fix a limit which shall indicate (when such is the case) that the supply of phosphatic manure is unnecessary is a more difficult question to decide. The soils of the various super-phosphate-manured wheat plots in Broadbalk Field, like those of the corresponding barley plots in Hoos Field, have been abundantly or over-abundantly supplied, and would probably grow undiminished crops for some years to come if the annual supply of phosphatic manure ceased, nitrogen (and other materials) being supplied as usual. Those included in our series average from ·04 to ·05 per cent. of citric-acid-soluble phosphoric acid—almost identically the averages found for the various corresponding barley soils. That this is indicative of superabundance of phosphates is evident from the fact that another plot (not analytically examined) receiving the same dressing of mineral manures, but receiving half as much again ot nitrogen (600 lbs. ammonium salts per acre) has consistently yielded considerably larger crops. We seem thus in a position to say that the limit of phosphatic sufficiency, for cereal crops, is somewhere below ·04 per cent. of citric-acid-soluble phosphoric acid, while as little as about ·01 per cent. indicates phosphatic starvation.

The plot 2 B, continuously dunged for 50 years, gives ·056 per cent., and is probably saturated with mineral constituents of plant food. Its yield is inferior to that of the most liberally manured chemical plot of the field (not represented in our table), owing, it may be supposed, to an insufficient annual supply of nitrogen in a rapidly available form.

Plot 2 A has been dunged for over nine years. Previously, for nearly thirty-five years, it was unmanured, except for partial dressings of alkaline sulphates. Its yield is about equal to the average of the chemically manured plots included in our table, though inferior to the best of them. It contains ·03 per cent. of citric-acid-soluble phosphoric acid. From various considerations it appears probable that the lower yield of plot 2 A, as compared with the much longer dunged plot 2 B, is rather due to a deficiency in the yearly supply of available nitrogen than to deficiency in the present supply of mineral food. If this were the case our limit indicative of phosphatic sufficiency would be reduced from ·04 to ·03 per cent. of citric-acid-soluble phosphoric acid.

This is, perhaps, as far as the results of the present enquiry carry us in this particular direction.

But it must not be forgotten that the crops in relation to which the results have been considered, both in this and in the earlier investigation, are both cereals; and it is quite possible that, for root crops, for instance, a higher minimum limit would be found to indicate phosphatic hunger.

Examination of the Results obtained from the Samples taken at various Depths of each Plot and in different Years.

We now proceed to an aspect of the results that is more complicated and more difficult to interpret. Some of the difficulties and complications that beset us have been already alluded to in introducing the subject, but one that has not been alluded to must be here pointed out, viz., that the 1865 samples and the 1881 samples were respectively twenty-eight and twelve years old when this investigation was taken in hand. As far as the total percentage of phosphoric acid is concerned, the age of the soil clearly makes no difference. But when the citric-acid-soluble phosphoric acid is considered, it is important to bear in mind that, while the numbers for the 1893 soils represent the citric-acid-soluble phosphoric acid obtained from the samples while yet fresh, the numbers obtained for the 1865 and 1881 samples do not tell us what was the citric-acid-soluble phosphoric acid in 1865 or in 1881, but only how much remains soluble after the dry soils have been kept stored in the laboratory through all the intervening years. Seeing that the soil is a highly complex mass, containing a quantity of silicates and of more or less free basic oxides, with a relatively minute quantity of salts, there is no knowing what chemical interchanges may have taken place in the course of time. Certainly by no means the whole of the surplus phosphoric acid supplied to the soil remains in a citric-acid-soluble condition; some of it reverts into some less soluble form. How far such change follows rapidly on its application, or how far it is the work of time, we cannot very well tell. The numbers obtained for the earlier samples, therefore, must be regarded cautiously, in view of the fact that they are not strictly comparable with the numbers for the 1893 samples, which were obtained while the samples were yet fresh.

Plot 3 (*Unmanured*).

This plot has had no manure whatever since the beginning of the experiments in 1844. Its yield from 1852 to 1893 averaged $12\frac{3}{4}$ bushels of wheat and $10\frac{5}{8}$ cwts. of straw per acre. From 1889 to 1894 the average was $13\frac{1}{8}$ bushels of wheat and $9\frac{1}{8}$ cwts. of straw.

The quantity of phosphoric acid removed in the crops during the fifty years, estimated from the periodical analyses of the ashes of the crops, is as follows, viz. :—

From 1844 to 1865, 249 lbs.
„ 1844 to 1881, 376 „
„ 1844 to 1893, 467 „

The analyses of the surface soil samples of 1865, 1881, and 1893, show a progressive diminution of total phosphoric acid; but the diminution shown is not in proportion to the removal, being considerably greater. In the second and third depths the variations in total phosphoric acid are so great as to be plainly due to natural

irregularity in the subsoils sampled. Such irregularities of either soil or subsoil, however, would probably have less effect on the citric-acid-soluble constituents.

We do not, however, find in this case a regularly progressive loss, though it is to be recollected that the determinations in the earlier samples were made, not at the time of sampling, but recently.

The citric-acid-soluble phosphoric acid in the samples taken in the three different years was found to be as follows :—

PLOT 3.—Phosphoric Acid dissolved by 1 per cent. Citric Acid Solution.

	Lbs. per acre.		
	1865.	1881.	1893.
First 9 inches	244	192	202
Second 9 inches	78	53	110
Third 9 inches	34	34	59
	356	279	371

The total difference in the numbers for the whole 27 inches between 1865 and 1881 is 77 lbs. per acre, which is nearly two-thirds of the quantity (127 lbs.) estimated to have been actually removed by the crops. During the next period, however, viz., from 1881 to 1893, we find, in the whole 27 inches, an increased quantity of citric-acid-soluble phosphoric acid, whereas the crops actually removed 91 lbs. per acre of phosphoric acid. Practically, in the surface soil, the quantity of citric-acid-soluble phosphoric acid would seem to have become stationary, while that in the subsoil has increased.

Comparing the 1893 samples with those of 1865, there is a loss of 42 lbs. of citric-acid-soluble phosphoric acid in the surface soil, a gain of 32 lbs. in the 2nd depth, and a gain of 25 lbs. in the 3rd depth. It is to be remembered that in 1865 the soil had already been for over twenty years unmanured, and its average cropping for the twenty years had then become reduced to less than 16 bushels of wheat per acre. The exhaustion from which it was at that time suffering, however, was mainly lack of available nitrogen, for Plot 10A, manured only with ammonium salts for most of the time, was giving an average crop half as great again. That Plot 3 was suffering also from lack of "mineral" food there is, of course, no doubt. But during the last thirty years the available mineral food as well as the available nitrogen of the soil must have been much more severely taxed ; and while this would readily explain the diminution of citric-soluble phosphoric acid between 1865 and 1881, or 1865 and 1893, in the surface soil, we should expect to find also a diminution in the second and third depths, whereas we actually find an increase. A possible explanation that suggests itself is that, as the surface soil has grown more exhausted,

the roots of the wheat have taken to deeper feeding, and have left more root residue in the subsoil in the later years.   An increased quantity of such remains would include an increased quantity of phosphoric acid in an easily soluble form.   At all events it is only the surface soil that shows impoverishment in citric-acid-soluble phosphoric acid between 1865 and 1893 ; and this impoverishment appears to have ceased since 1881.   In the second and third depths the impoverishment shown in 1881 has been since succeeded by a gain.   Even this impoverished soil now contains in the 27 inches over 8600 lbs. per acre of *total* phosphoric acid, most of which (as is amply evidenced by the history of other plots) is, for present purposes, practically useless as plant food.

Plot 4 (*Unmanured since* 1852).

Since 1852, *i.e.*, for forty-two years up to the time of the last sampling, this plot, like Plot 3, has been unmanured.   But prior to 1852 it was annually dressed with bone-ash superphosphate and ammonium sulphate.   For all practical purposes it is now almost as starved out as Plot 3, though, when the yields of the two are compared in detail, it is found that, in virtue of its liberal mineral treatment more than forty years earlier, Plot 4 has yielded a slightly better average crop than Plot 3, viz., $13\frac{1}{2}$ bushels of grain per acre as against the $12\frac{3}{4}$ bushels of No. 3—a difference still nearly maintained, for the average yield from 1889 to 1894 was $\frac{3}{8}$ bushel better than that of Plot 3.   The average yield of straw for forty years has also been slightly heavier.

It is of interest to see if this slight but still persistent difference in fertility, dependent upon treatment forty years ago, would prove to be accompanied by any difference analytically apparent in the mineral contents of the soil, when compared with Plot 3 ; but only the 1893 samples were examined.

Plot 3 is estimated to have lost in cropping in fifty years 467 lbs. of phosphoric acid.   Plot 4 has yielded in the same time 528 lbs., but received in earlier years 506 lbs. in manure.   Hence, the soil of Plot 4 should contain 445 lbs. per acre more phosphoric acid than that of Plot 3.

Phosphoric Acid (lbs. per acre).

Depth.	Plot 3. (1893.)		Plot 4. (1893.)		Plot 4 more or less than Plot 3.		
					Found.		Estimated.
	Total.	Citric soluble.	Total.	Citric soluble.	Total.	Citric soluble.	
First 9 inches .	2956	202	3111	260	+ 155	+ 58	
Second 9 inches.	3019	110	2832	64	− 187	− 46	+ 445 lbs. per
Third 9 inches .	2708	59	2708	48	—	− 11	acre

For reasons already discussed not much stress is to be laid on the 2nd and 3rd depths, as regards total phosphoric acid, when differences so relatively fine as this are concerned.   But it is to be noted that about one-third of the estimated excess is found in the total phosphoric acid in the surface soil, and that there is still a tangible difference, viz., 58 lbs. per acre, between the citric-acid-soluble phosphoric acid contents of the surface soils, seeming to show that the mineral resources of the surface soil have been less severely strained.   This 58 lbs. is 40 per cent. of the " total" difference actually found between the two surface soils.   The citric-acid-soluble phosphoric acid in the subsoil is, however, less, and the numbers are more like those found for the 1865 samples of Plot 3, indicating possibly (see observations on Plot 3) that the crops have left less root residue in the lower depths in the less starved soil.

Reducing the numbers for the surface soils to unit ratio, we find the ratio for total phosphoric acid in the two surface soils 3 and 4 is as 1 : 1·05, while for citric-acid-soluble phosphoric acid it is as 1 : 1·29.

Qualitatively, therefore, a distinct difference is indicated in phosphatic fertility, due to differences in manuring more than forty years earlier.

Plots 10 (A *and* B) (*Ammonium Salts only*).

Plot 10 has received during nearly the whole of its history 400 lbs. per annum of ammonium salts, with no mineral manures at all since 1850.   The plot is divided into two "lands," A and B, treated as separate plots.   Plot 10A received a dressing of mineral manure, including 82 lbs. of phosphoric acid, in 1844, but none since. Plot 10B received mineral dressings in 1844, 1848 and 1850, including 210 lbs. of phosphoric acid.   The effect of the extra mineral dressings on Plot 10B is apparent down to the present time, as will be seem from the following records.

	Average yield per acre for 42 years (1852–93).		Average yield per acre for 6 years (1889–94).	
	Wheat (bushels).	Straw (cwt.).	Wheat (bushels).	Straw (cwt.).
Plot 10A . . .	$19\frac{1}{2}$	$17\frac{3}{4}$	$16\frac{1}{2}$	$13\frac{1}{2}$
Plot 10B . . .	$21\frac{7}{8}$	20	18	$15\frac{1}{4}$

Samples of the soil representing 10A in 1865, 1881 and 1893, have been examined, and samples representing 10B in 1881 and 1893.   The samples representing the 2nd and 3rd depths are evidently too irregular to have any precise significance, as far as regards total phosphoric acid, though they are important as regards citric-soluble contents.

The following tables show the quantities of phosphoric acid per acre calculated from the analyses, the differences found on comparison, and the actual losses estimated from the known additions and crop removals.

Plots 10A and 10B.

Total Phosphoric Acid (lbs. per acre).

		Plot 10A.	Plot 10B.	Excess (B over A) found in B.	Excess per acre estimated from actual additions to soil and removals in crops.
		Lbs.	Lbs.	Lbs.	Lbs.
1865.	1st 9 inches . .	3785	—	—	96
1881.	,, ,, . .	3267	3370	103	72
1893.	,, ,, . .	3189	3267	78	60

Citric Acid soluble Phosphoric Acid (lbs. per acre).

		Plot 10A.	Plot 10B.	Excess (B over A) found in B.	Excess of total phosphoric acid per acre estimated from actual additions to soil and removals in crops.
		Lbs.	Lbs.	Lbs.	Lbs.
1865.	1st 9 inches . .	275	—	—	—
,,	2nd ,, . .	83	—	—	—
,,	3rd ,, . .	39	—	—	—
		397	—	—	96
1881.	1st 9 inches . .	176	239	63	—
,,	2nd ,, . .	48	75	27	—
,,	3rd ,, . .	36	34	− 2	—
		260	348	88	72
1893.	1st 9 inches . .	192	192	0	—
,,	2nd ,, . .	83	115	32	—
,,	3rd ,, . .	50	59	9	—
		325	366	41	60

Here we find both in 1881 and in 1893 that the total phosphoric acid found in the surface soil in the two plots corresponds fairly closely with the estimated difference. In 1881 the estimated difference accords very closely with the difference found in citric-acid-soluble phosphoric acid in the first 9 inches, but in 1893 the citric-acid-soluble difference in the surface soils is no longer found, the two surface soils being alike. But two-thirds of the estimated excess is found in the second and third depths.

Although the differences in citric-acid-soluble phosphoric acid for the whole

27 inches so nearly correspond with the estimated excess of phosphoric acid per acre, it will be seen that the citric-acid-soluble phosphoric acid in 10A, after decreasing greatly between 1865 and 1881, seems since to have risen, especially in the lower depths; and that that in 10B, during the latter period, having decreased largely in the surface soil, has risen in the subsoil to almost the same extent. Each plot between 1881 and 1893 yielded in its crops nearly 109 lbs. per acre of phosphoric acid (10A, 97 lbs., and 10B, 109 lbs.), a loss which is approximately indicated in the total phosphoric acid of the surface soil. This loss is not, however, indicated in the citric-acid-soluble figures for Plot 10A. On Plot 10B rather less than half the loss is seen in the citric-soluble for the first depth, but it is made up for by the increase in the subsoil. Both surface soils, in fact, have sunk to the same low level, in citric-acid-soluble phosphoric acid, as the continuously unmanured Plot 3, or slightly below it, the quantity in 10A being distinctly lower than that in Plot 3 in the second depth, while 10B is slightly higher. All three soils would seem to have reached the stage at which the surface soils maintain a fairly constant minimum of citric-soluble phosphoric acid, probably dependent mainly on the annual decay of the crop residues, viz., roots and stubble; while the quantity in the subsoil has, during recent years, been probably reinforced by an increase of deep root-growth, as the roots have to extend their feeding area—not merely to obtain phosphoric acid, but in the case of Plot 3 to get nitrogen, and in the case of both 3 and 10 to get potash and other minerals.

Plot 3, 10A *and* 10B *Compared.*

The following tables show the diminutions of phosphoric acid—total and citric-acid-soluble—as indicated in the samples taken at the three periods, side by side with the diminutions per acre estimated from manurial additions and the weight and composition of the crops.

Loss (—) or Gain (+) in

Total Phosphoric Acid, 1st 9 inches (lbs. per acre).

Plot.	From 1865 to 1881.		From 1881 to 1893.		From 1865 to 1893.	
	Found by analysis.	Estimated.	Found by analysis.	Estimated.	Found by analysis.	Estimated.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
3	− 234	− 127	− 440	− 91	− 674	− 218
10A	− 518	− 159	− 78	− 97	− 596	− 256
10B	—	− 182	− 103	− 110	—	− 292

Loss (−) or Gain (+) in

Citric-acid-soluble Phosphoric Acid (lb. per acre).

	From 1865 to 1881.		From 1881 to 1893.		From 1865 to 1893.	
	Found by analysis.	Estimated.	Found by analysis.	Estimated.	Found by analysis.	Estimated.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Plot 3—						
1st 9 inches	− 52	—	+ 10	—	− 42	—
2nd ,,	− 24	—	+ 56	—	+ 32	—
3rd ,,	—	—	+ 25	—	+ 25	—
27 inches	− 76	− 127	+ 91	− 91	+ 15	− 218
Plot 10A—						
1st 9 inches	− 99	—	+ 16	—	− 83	—
2nd ,,	− 35	—	+ 35	—	0	—
3rd ,,	− 3	—	+ 14	—	+ 11	—
27 inches	− 137	− 159	+ 65	− 97	− 72	− 256
Plot 10B—						
1st 9 inches	—	—	− 47	—	—	—
2nd ,,	—	—	+ 40	—	—	—
3rd ,,	—	—	+ 25	—	—	—
27 inches	—	− 182	+ 18	− 110	—	− 292

In the case, then, of Plot 3 the samples, even of the surface soils, of the various years—presumably owing to natural irregularities—do not show quantities of total phosphoric acid quantitatively corresponding to the removals for each period, though the differences are in the direction of progressive diminution. In the case of 10A, the difference found between the 1865 and 1883 samples (and hence between those of 1865 and 1893) is also too great; but the difference between the 1881 and 1893 samples corresponds almost quantitatively with the estimated loss, as does also the difference found between the corresponding samples of Plot 10B.

When the citric-acid-soluble phosphoric acid results are similarly regarded we find, in comparing the 1865 and 1881 samples, that in the case of Plot 3 60 per cent. of the estimated loss is represented by the diminution of citric-acid-soluble phosphoric acid in the first 18 inches, and in the case of Plot 10A over 85 per cent. Between 1881 and 1893, however, it is only in 10B that the store of citric-acid-soluble phosphoric acid shows diminution, Plots 3 and 10A in all three depths, and even Plot 10B in its lower depths, showing, despite continued crop losses, a small but distinct increase.   This has already been commented upon, and it is to be remembered that our comparisons only deal with samples taken during the latter half of the history of the plot.   Unfortunately we have no samples of the soil drawn in 1843 to

compare with those of 1865 and later, and do not know what was the initial quantity of citric-acid-soluble phosphoric acid in either soil or subsoils.

Plots manured with Phosphates (Nos. 7, 13, 14, 12, 11, and 5).

So far we have examined the results of only the plots not manured with phosphates. We now turn to the interesting series of plots which have been for fifty years continuously dressed with superphosphate (3½ cwts. per acre annually).

For the more precise details of the manuring of each of these plots the reader is referred to p. 238.

Briefly, they may be thus summarised :—

Annual Manuring.

Plot 7. Ammonium salts, Phosphates, Potassium, Sodium, and Magnesium salts.
   „   13.   „   „   „   and Potassium salts.
   „   14.   „   „   „   and Magnesium salts.
   „   12.   „   „   „   and Sodium salts.
   „   11.   „   „   and Phosphates.
   „   5. Phosphates, Potassium, Sodium, and Magnesium salts.

In the first eight years prior to 1852 the treatment was somewhat irregular in the case of some of the plots. For instance, Plots 14 and 12 received some dressing of potassium salts, and Plot 11 a dressing of rape cake. But since 1852 the treatment has been regular.

The quantity of ammonium salts is 400 lbs. per annum. This quantity, as is shown by comparison with another plot receiving 600 lbs. ammonium salts yearly, and the same minerals, is insufficient to produce the maximum crop that the soil will afford. Hence it is evident the phosphatic dressing annually supplied is more than sufficient to keep pace with the nitrogenous supply of the series now under consideration, and that the differences between the productivity of these plots (except 5) are due to the influence or absence of the various salts other than phosphates and ammonium salts.

The annual supply of phosphoric acid being known, and the annual removal being calculable from the weight of the produce and from the periodical ash analyses of that of each separate plot, we are able to calculate the accumulation of phosphoric acid per acre on each plot. We have now to see how far the calculated accumulations are found to be actually represented in the various soils at various periods and in various depths.

Briefly, it may be said that the surface soils in their varying proportions of total phosphoric acid are substantially in accord with expectation. In order to compare the accumulation of phosphoric acid found with that expected it is necessary to take

some fixed plot as a standard. The plot that naturally suggests itself is the unmanured Plot 3. If the loss of phosphoric acid by cropping on this plot, during each period, is added to the calculated accumulation on each of the other plots, we get the calculated excess of phosphoric acid per acre in each of these plots over and above the quantity still left in Plot 3. These calculations are necessarily based on the assumption that all the plots originally contained the same quantity of phosphoric acid per acre. This may or may not be an approximately true assumption for the first 9 inches of soil—but the inequalities in the samples from the lower depths render it improbable that there is very much regularity in the subsoil distribution, and make quantitative comparisons or conclusions as to accumulation or diminution in the second and third depths of the various plots impracticable as far as regards total phosphoric acid.

With citric-acid-soluble phosphoric acid the case is different.

The following table shows the calculated excess of phosphoric acid per acre in each plot (as compared with Plot 3); the excess of total phosphoric acid (as compared with Plot 3) actually found in the first 9 inches; and the excess or deficiency of citric-acid-soluble phosphoric acid (again as compared with Plot 3) in the three depths of soil respectively, and in the total 27 inches comprised by them. The results are given for the three periods of 22, 38, and 50 years which had elapsed between the beginning of the experiments and the respective dates of sampling.

A study of this table shows that the greater part of the calculated excess of phosphoric acid per acre is found in the surface soil. In the 1865 samples from 76 to 96 per cent. of the calculated accumulation is found in the first 9 inches; in the 1885 samples, from 66 to 89 per cent., and in the 1893 samples from 78 to 91 per cent. It would appear that in the course of years some of the phosphoric acid has descended lower—but at the same time the reader may be again reminded that the accumulations are calculated on the supposition that the soils were all originally alike in phosphoric acid contents, and further, that most of the deficit between the calculated accumulations and those actually found in the surface soil are comprised within a difference equal to only ·01 per cent. on the soil. Nevertheless, as the difference is always in the direction of deficiency, it seems probable that on the whole it is attributable to descent. Unfortunately the natural variations in total phosphoric acid in the subsoils are too great to enable us to verify subsoil accumulation.

Plots 7, 13, 14, 12, 11 and 5.

Plot.	Estimated excess of phosphoric acid over Plot 3, calculated from known additions and removals. lbs. per acre.	Excess of total phosphoric acid over Plot 3, found by analysis in 1st 9 inches of soil. lbs. per acre.	Excess (+) or deficiency (−) of phosphoric acid soluble in 1 per cent. citric acid solution, as compared with Plot 3. lbs. per acre.			
			1st 9 inches.	2nd 9 inches.	3rd 9 inches.	Whole. 27 inches.
After 22 years (1844–1865).						
13	1161	881	+ 433	− 19	0	+ 414
14	1198	985	+ 423	− 13	+ 14	+ 424
12	1161	1114	+ 451	− 27	+ 6	+ 430
11	1175	959	+ 428	− 19	+ 14	+ 423
After 38 years (1844–1881).						
13	1985	1763	+ 801	− 3	− 6	+ 792
14	2045	1504	+ 752	− 11	− 3	+ 738
12	2019	1789	+ 809	0	0	+ 809
11	2081	1374	+ 661	− 8	0	+ 653
After 50 years (1844–1893).						
7	2452	2100	+ 1216	− 8	+ 25	+ 1233
13	2587	2359	+ 923	− 37	− 14	+ 872
14	2667	2333	+ 944	− 48	+ 6	+ 902
12	2651	2255	+ 869	− 16	− 3	+ 850
11	2759	2151	+ 848	− 35	− 11	+ 802
5	3049	2722	+ 1462	+ 29	+ 42	+ 1533

Broadly speaking, the results of the analyses show beyond doubt that the unused phosphates, though applied in the soluble form, are mainly retained near the surface.

A more interesting question, however, is, as to the form in which the excess is to be found. Of the total phosphates added to the soil, probably nine-tenths would be in a condition originally soluble in weak citric acid; but the unused portion even of the originally soluble phosphate would enter into more or less firm combination with the bases of the soil, as shown by the retention of its main bulk in the surface soil. It is, however, a matter of great interest to see how much of the accumulated quantity is to be still found in the condition of ready solubility in weak citric acid and how it is distributed as regards depth. Of the quantity found a part will be due, no doubt, to root and stubble residue, but in these plots the main portion, in the surface soil, may be taken as due to unappropriated manure.

If we take the figures of the last tables, in which throughout the figures of the unmanured plot No. 3 are deducted, so as to show only the excess found, it will be seen that in the 1865 samples the first 9 inches of soil showed that from 35 to 39 of the calculated total excess of phosphoric acid existed therein in the citric-acid-soluble form. In the 1881 samples the proportion of calculated excess so found was from 32 to 40 per cent., and in 1893 from 31 to 36 per cent. for the corresponding plots, and 48 and 50 per cent. for the two other plots not sampled in the earlier years.

In the second depths of 9 inches, however, at none of the periods do we find more citric-acid-soluble phosphoric acid than in the totally unmanured Plot 3. In fact, we find actually less in every instance but one.

In the third depths, too, there is a slight excess, on the whole, in the 1865 samples ; and in the 1893 samples an excess only in three cases, and in only two of these is the excess a fairly tangible one.

Now it has already been seen that there is reason to suppose that there has been a descent of manurial phosphoric acid below the first 9 inches. Why is practically none of it found there, in four at least of the six plots, in a citric-soluble condition ? And, further, why is there on the other hand, notwithstanding the downward transmission of phosphates, an actual deficiency of phosphoric acid in a presumably available condition ? The explanation that suggests itself is, that while much of such phosphoric acid as has gone down may well have reverted into an insoluble condition, there has, as compared with the state of things on the unmanured plot, been a much more vigorous plant-growth on these plots, manured with both nitrogen and phosphates (and some of them with alkalies also), with the effect that the roots have fed more vigorously in the second and third depths of the soil, producing a greater strain on the phosphoric acid resources of the subsoil, notwithstanding the abundance of phosphatic food above. Although the total percentages of phosphoric acid in the subsoil samples are not to be regarded (for reasons already discussed) with much confidence, whether comparing plot with plot, or period with period, it may nevertheless be noted that in the third depths—19 to 27 inches—the total phosphoric acid for the three separate periods is found to diminish from period to period in the case of the Plots 11, 12, 13 and 14, manured with phosphates and nitrogen, there being only one among these twelve subsoil samples that breaks the otherwise regular gradation. This seems to suggest that any phosphates which have descended below the first 9 inches have not travelled as far as the third depths, but that the crops have been feeding in these lower depths and diminishing the store of phosphoric acid therein. But having regard to the obvious irregularities of composition of some of the other subsoils, it may be well not to dwell too strongly on the significance of the certainly striking diminution of the phosphoric acid shown from period to period in the lower subsoil samples of these plots.

Effect of Alkaline Salts on the Solubility of Phosphoric Acid in the Soil.

It will have been seen that two of the six phosphate manured plots differ notably from the others in the subsoil contents of citric-acid-soluble phosphoric acid. These are Plots 5 and 7. These two plots alone, in addition to phosphoric acid, have had persistently supplied to them potassium, sodium, and magnesium salts (400 lbs. per annum in the aggregate). To three of the other four plots one or other of these salts has been supplied, but only to these two have *all three* salts been given. One of the two (Plot 7) has received ammonium salts also in the same quantities as Plots 11 to 14. The other (Plot 5) has received the same full phosphatic and mineral saline dressing, but without ammonium salts.

Plot 5, getting no nitrogen, and yielding in consequence an annual average crop not very greatly exceeding that of the unmanured soil, has naturally accumulated a far larger quantity of phosphoric acid, nearly 500 lbs. more per acre being found by analysis in the first 9 inches than in the average of the plots receiving both ammonium salts and mineral manures. As would be expected, there is also a much larger accumulation of citric-acid-soluble phosphoric acid, and the proportion of citric-acid-soluble to total accumulation is greater than in the average of these other plots· Further, in both the second and third depths we find a tangible excess of citric-acid-soluble phosphoric acid beyond that in the unmanured plot, showing that the available phosphoric acid in the subsoil has been in excess of the demands of the crops. That this is not wholly due to the supply of a relatively large abundance of phosphoric acid without nitrogen, but also to another cause, appears on comparison with the results found in the case of Plot 7, which in addition to a precisely similar liberal supply of phosphates and other saline minerals, has received also ammonium salts.

Plot 7 has yielded, in virtue of the full supply of potassium, sodium and magnesium salts, in addition to phosphates and ammonium salts, a persistently larger yield of both wheat and straw than any of its companions. Consequently, its output of phosphates has been greater, and its accumulation less. Instead, however, of being poorer in " available " phosphoric acid, it is now richer to the extent of some hundreds of pounds per acre than its companions which received either less alkaline salts or none.

It is also, as regards citric-acid-soluble phosphoric acid, appreciably richer than the said plots in the second and third depths, though not to the same extent as Plot 5.

It seems that the full supply of potassium, sodium and magnesium salts has either exerted a solvent action on the natural store of otherwise unavailable phosphoric acid in the soil, or, which appears more probable, that the manurial phosphates have entered into combination with the saline bases, and been retained in a less insoluble condition than where these have been absent or less in quantity.

Plot 11, which has received phosphates and ammonium salts only, and has yielded smaller crops and accumulated more phosphates than Plots 12, 13 and 14, shows less

citric-acid-soluble phosphoric acid than any of them.   Next comes Plot 12, which has annually received 366½ lbs. per annum of sodium sulphate, and which, though accumulating less phosphoric acid, is nevertheless appreciably richer in citric-acid-soluble.   Next is Plot 14, accumulating almost the same phosphoric acid as Plot 12, but getting 280 lbs. per annum of magnesium sulphate, and showing, in the surface soil, 75 lbs. more of citric-soluble phosphoric acid, though less in the subsoil.   Next come Plots 13 and 14, getting respectively 200 lbs. of potassium sulphate and 280 lbs. of magnesium sulphate per annum.   These have accumulated respectively 64 lbs. less and 16 lbs. more of phosphoric acid per acre than Plot 12, but are respectively 55 lbs. and 75 lbs. richer in citric-acid-soluble in the first 9 inches.

The following figures show the proportion borne by the excess of citric-acid-soluble phosphoric acid over Plot 3 (both in the first 9 inches and in the whole 27 inches) to the calculated accumulated excess over Plot 3.

1893 Samples.

Plot.		Ratio of excess of citric-acid-soluble phosphoric acid over unmanured plot to calculated excess of phosphoric acid supplied per acre over unmanured plot, the calculated excess in each case being taken as 100.	
		First 9 inches.	27 inches.
5	Phosphates, potassium, sodium, and magnesium salts	48 per cent.	50 per cent.
7	Ammonium salts, phosphates, potassium, sodium and magnesium salts	50 ,,	50 ,,
13	Ammonium salts, phosphates and potassium salts	36 ,,	34 ,,
14	Ammonium salts, phosphates and magnesium salts	35 ,,	34 ,,
12	Ammonium salts, phosphates and sodium salts	33 ,,	32 ,,
11	Ammonium salts and phosphates only	31 ,,	29 ,,

It appears that the action of sodium sulphate (366 lbs. per annum) in maintaining the phosphate in an easily soluble condition has been somewhat less than that of magnesium sulphate (280 lbs. per annum), and that this again has had less effect than potassium sulphate (200 lbs. per annum).   But the addition to the 200 lbs. of potassium sulphate of 100 lbs. magnesium sulphate, and 100 lbs. sodium sulphate,

has greatly affected the condition of the phosphoric acid in the surface soil, and has appreciably affected it in the subsoil.

The Dunged Plots (2A and 2B).

Plot 2B, it will be remembered, has yearly received since 1843 a dressing of 14 tons per acre of farmyard manure. Plot 2A was unmanured from 1849 to 1883, except that a portion of it received alkaline salts. Since 1883 it has received the same treatment as Plot 2B, viz., 14 tons of dung per annum. The former plot has yielded on the average, for fifty years, over $34\frac{5}{8}$ bushels of wheat and $32\frac{1}{4}$ cwt. of straw per acre, a better yield than that of any of the other plots already considered, though inferior to that of another plot (No. 8) already alluded to, which, in addition to a full dressing of mineral manures, has received 600 lbs. of ammonium salts per annum.

During the last six years of the period of fifty years which we are considering, Plot 2B yielded $40\frac{7}{8}$ bushels of grain per annum and $38\frac{3}{4}$ cwt. of straw, while Plot 7 (400 lb. of ammonium salts, with full minerals) averaged only $34\frac{3}{4}$ bushels of wheat and $33\frac{5}{8}$ cwts. of straw. During the same six years Plot 2A averaged $30\frac{1}{4}$ bushels of wheat and $28\frac{3}{8}$ cwt. of straw. Clearly, therefore, Plot 2B has reached, as would be expected, a state of high fertility, while Plot 2A, though, at the time of the last soil sampling, it had for nine years received the same treatment as 2B, was, nevertheless, far behind it in fertility, the previous forty years of dung still telling very markedly on the latter plot. It is much more difficult to estimate the yearly addition of phosphoric acid to the dunged plots than to estimate it in the case of the chemically manured plots; for the phosphatic manures are of fairly definite and uniform composition, while dung is necessarily variable and is very difficult to sample in such a way as to get an analysis, even for one yearly application, which may be assumed to fairly represent the 14 tons applied. The estimate that can be made is therefore at the best to be regarded as only an approximation, the degree of which is unknown. Sir HENRY GILBERT considers that on the whole it may be fairly estimated that the dung applied contains 0·25 per cent. of phosphoric acid, and since this small percentage represents in fifty years 3920 lb. per acre, it is clear that there is room in the estimate for considerable error. If the estimate of 0·25 were 0·05 too high or too low as compared with the real average percentage in a material of so indefinite and so fluctuating a composition as farmyard manure, the error of estimate on the fifty years would amount to nearly 800 lb. This must be borne in mind in the quantitative consideration of the analytical results.

In the following table the estimate of 0·25 per cent. is taken for the phosphoric acid in the dung.

Plot 3 (continually unmanured) is again taken as a standard, the sum of the estimated loss of phosphoric acid per acre on Plot 3 and of the estimated gain on Plot 2B representing the estimated excess of phosphoric acid per acre in the latter plot.

Plot 2B (Dunged for Fifty Years).

	After twenty-two years (1844–1865).	After thirty-eight years (1844–1881).	After fifty years (1844–1893).
	lbs. per acre.	lbs. per acre.	lbs. per acre.
Estimated excess of total phosphoric acid per acre over Plot 3	1427	2410	3086
Excess of total phosphoric acid per acre over that in Plot 3 found by analysis in first 9 inches	1055	1252	2062
Excess of phosphoric acid (as compared with Plot 3) soluble in 1 per cent. solution of citric acid found in :—			
First 9 inches	636	699	1105
Second 9 inches	40	30	141
Third 9 inches	8	14	36
27 inches	684	743	1282

Regarding first the total phosphoric acid, it is evident that if the estimates of accumulations are approximately correct, a very much larger quantity of the phosphoric acid, supplied in the form of dung, must have descended into the subsoil than we have seen to be the case on the plots manured with superphosphate. In the 1865 samples little more than two-thirds of the expected excess is found by analysis in the top 9 inches of soil; in the 1881 samples not much more than half, and in the 1893 samples only about two-thirds. Even if we allow some considerable margin for possible error in the estimated accumulation, it still appears clear that there must have been considerable descent. Unfortunately the irregularity of composition of the subsoils, to which reference has so often been made, makes it very difficult to trace the descent quantitatively. If we regard the total phosphoric acid in the samples of the second 9 inches we find on Plot 2B, as compared with Plot 3, an excess of 267 lbs. in 1865 and 481 lbs. in 1881—figures which would, as far as they go, account for much of the descended phosphates. But the sample of the second 9 inches drawn in 1893 shows, as compared with that of Plot 3, actually a slight deficiency, and a comparison between the figures of each set of samples of the second 9 inches makes it clear that some at least of these samples cannot be really representative of the plots, as they are inconsistent among themselves. The third depths, as has been stated before, are hopelessly irregular in total phosphoric acid.

The descent, however, of the phosphoric acid is qualitatively seen in the increase of citric-acid-soluble phosphoric acid in both the second and third depths, especially in the more recent samples.

In the citric-acid-soluble form in 1865, 1881, and 1893 respectively, we find, in the whole 27 inches, 48 per cent., 31 per cent., and 41 per cent. of the expected excess

of phosphoric acid. Of the excess of total phosphoric acid actually found arrested in the first 9 inches, considerably more than one-half exists in the citric-soluble state—forming a large reserve of phosphatic fertility. This reserve, as we have seen, is far from being confined to the subsoil, though much of the phosphoric acid which must be supposed to have descended into the subsoil has evidently assumed a less available form.

It is interesting to speculate as to the cause of this greater descent of phosphoric acid into the subsoil in the case of the dunged as compared with the artificially manured plots. Is the reason a merely chemical one—as in the case of Plots 5 and 7, where potassium, sodium, and magnesium salts are used in conjunction with superphosphate and have so markedly influenced the condition of the phosphoric acid as compared with that of the plot in which superphosphate is used without such aid ? Or is it not possible that earth-worms may play a part in the distribution of the constituents of the dung by devouring it and conveying it downwards—in the same way that they are well known to take down leaves and other vegetable substances ?

Plot 2A (*Dunged for Nine Years only*).

This plot had at the time of sampling the soil only been dunged for nine years. Its condition had previously been that of Plot 3. We will examine its results in the same way as we have examined those of the companion plot—this plot being particularly interesting, having been restored to a fertile condition after forty years of nearly complete starvation.

PLOT 2A.—(Dunged for nine years; unmanured for previous forty-one years.)

	lbs. per acre.
Estimated excess of phosphoric acid per acre over Plot 3	592
Excess of total phosphoric acid over that in Plot 3 found by analysis in the first 9 inches	1186
Ditto in first 18 inches	705
Ditto in first 27 inches	342
Excess of phosphoric acid over Plot 3 soluble in 1 per cent. solution of citric acid found in :—	
First 9 inches	604
Second 9 inches	29
Third 9 inches	19
27 inches	652

The excess of phosphoric acid in the surface soil in this case is much more than the calculated excess per acre—being in fact a good deal more than the total phosphoric acid supposed to be contained in the dung used. It is noteworthy,

however, that the lower depths of this plot are markedly *poorer* in total phosphoric acid than those of Plot 3—so that the excess nearly disappears if we calculate for 18 inches, and becomes a deficiency if we include the third 9 inches; but as no earlier samples have been examined there is no evidence to show whether the variation in the subsoils is (as is clear in many other cases) a mere accident.

The quantity of citric-acid-soluble phosphoric acid in this case appears to account for the estimated accumulation of dung phosphates, seeming to suggest that—even allowing for possible inaccurate representation of the soil by the sample—less of the dung phosphates have reverted to the insoluble condition than in the case of the older dung accumulations on 2B—which is what might be expected. The influence of the dung on the "available" phosphoric acid of the subsoil is—as might also be expected—much less marked than in the case of the soil dunged for fifty years, but is nevertheless apparent.

PHOSPHORIC ACID IN DRAINAGE WATERS.

(Analyses by the late Dr. A. VOELCKER.)   No evidence of substantial Loss.

A number of years ago, from 1866 to 1869, the late Dr. A. VOELCKER made detailed analyses of several series of samples of pipe drainage water collected from these plots. The results are given in a paper "On the Composition of Waters of Land Drainage" ('Journal of the Royal Agricultural Society of England,' 1874), and subsequently summarised in a Rothamsted paper "On the Rain and Drainage Waters at Rothamsted ('Journal of the Royal Agricultural Society of England,' vol. 18, Part I., 1882). These are the only fairly complete mineral analyses that have been made of the waters showing the various bases and acids present; though pretty constant examinations have for many years been made for nitric nitrogen and chlorine. Few as the analyses were, however, it is desirable that we should here inquire how far they bear upon the soil results discussed in the present paper.

The drain pipes, it should be mentioned, are situated at a depth of about 27 inches from the surface, or at about the bottom of the third depth of 9 inches.

The average quantities of phosphoric acid found in the various collections of drainage water from the plots with which we are concerned were as follows :—

	Average quantity of phosphoric acid in drainage water. Parts per million.
Plots 3 and 4 (unmanured)	0·63
Plot 10 (ammonium salts only)	1·44
„ 5 (full mineral dressing without nitrogen)	0·91
„ 7 (ammonium salts and full minerals)	0·91
„ 11 (ammonium salts and superphosphate)	1·66
„ 12 (ammonium salts, superphosphate and sodium sulphate) .	1·26
„ 13 (ammonium salts, superphosphate and potassium sulphate)	1·09
„ 14 (ammonium salts, superphosphate and magnesium sulphate)	1·01

The variations in the *average* phosphoric acid contents of the various samples collected from the pipes of each plot are from 0·63 part per million on the unmanured plots (3 and 4) to 1·66 parts per million on plot 11 (phosphates and ammonium salts). If we assume a downward percolation to this depth—either from the drain-pipes or into the subsoil—of 10 inches of drainage water per annum, 1 part per million of water corresponds, in round numbers, to a quantity of $2\frac{1}{4}$ lbs. per acre per annum. The average variations, then, would, in round numbers, be from $1\frac{1}{2}$ lbs. to $3\frac{3}{4}$ lbs. of phosphoric acid per acre per annum, the average quantity for all plots being $2\frac{1}{2}$ lb. per acre per annum.

Such differences as exist in the quantities of phosphoric acid found in the drainage waters from the various plots appear, in some cases, to bear a relation to the manuring and cropping conditions; but in other cases there are inconsistencies; and it is to be remembered that the actual quantities analytically dealt with amounted only to small fractions of a grain of phosphoric acid per gallon of water, and that the methods for the quantitative estimation of minute quantities of phosphoric acid were less satisfactory at that time than they are at the present day. So that not too much stress must be laid upon the differences found between individual plots or samples.

Substantially, the results seem to show that no very appreciable quantity of manurial phosphoric acid passes away annually in the drainage water. Of course, the annual descent, even of the average quantity of $2\frac{1}{4}$ lbs. per acre found in the drainage waters, would tell in course of time, amounting in fifty years to 1 cwt. of phosphoric acid per acre; but the difference between the losses from different plots probably would not materially influence the *comparative* phosphoric acid contents of the soils.

As far as the limited number of determinations made can be accepted as general evidence, it would seem that there is not a very great difference between the quantity of phosphoric acid then contained in the drainage water from the unmanured plots on the one hand, and from the plots manured with a superabundance of superphosphate on the other. The descent by drainage may, of course, have become somewhat greater in later years, as unutilised phosphates have accumulated.

It is a matter of regret that among the results we have no phosphoric acid determinations in the drainage water from the dunged plot 2B. This plot, owing to the absorptive character of its soil caused by the annual additions of organic matter, is so retentive of moisture that the drain-pipes very seldom run except in very wet weather, and Dr. VOELCKER was unable to obtain samples of drainage water from this plot when most of the other samples were collected.

SUMMARY AND GENERAL CONCLUSIONS AS TO PHOSPHORIC ACID.

On the whole, the results show that by far the greater portion of the unconsumed phosphoric acid added in manure is accumulated in the surface soil, although most of the phosphoric acid has been originally soluble in water, and its application has

extended over fifty years. By the surface soil is here meant the first 9 inches. In the case of dung, however, there is considerable descent into the second and third 9 inches. In the case of superphosphate accompanied by constant dressings of potassium, sodium, and magnesium salts, there is evidence of a tangible descent into the second, and even into the third, 9 inches. In the case of the chemically manured plots, however, the greater part of the calculated accumulation of phosphoric acid is found by analysis in the surface soil, and a large proportion of it is found in a condition in which it dissolves in a weak solution of citric acid. This reagent enables us to trace qualitatively the descent alluded to in the subsoils of certain of the plots.

While the differences between the total percentages of phosphoric acid in the surface soils of the variously manured and unmanured plots correspond, as a whole, fairly well with their history, the differences would by no means suffice, in the absence of a knowledge of such history, to give any adequate indication of the profound differences in phosphatic condition which we know to exist ; but the relative · proportions of citric-acid-soluble phosphoric acid appear to afford a striking index to the relative phosphatic fertility of the soils.

The probable limit denoting phosphatic deficiency for cereals seems to be, as deduced from this investigation, between $0·01$ and $0·03$ per cent. of citric-acid-soluble phosphoric acid in the surface soil. That is to say, a percentage as low as $0·01$ seems to denote an imperative demand for phosphatic manure, while as much as $0·03$ would seem to indicate that there is no such immediate necessity. For root crops, more especially turnips, the limits would probably be higher.

In the subsoil samples, the irregularities and variations in the natural or original phosphoric acid of the subsoils themselves are such that the total percentages tell us, as a rule, nothing ; while the citric acid results frequently show striking and consistent differences, and are also of considerable interest when studied in connection with the problems of root range and subsoil feeding.

The influence of alkaline salts on the retention of phosphoric acid in a less fixed and presumably more available condition is interesting, increasing as it does with increase of saline applications.

The superabundance of phosphoric acid estimated to have been supplied in dung over fifty years is less satisfactorily accounted for than is the case with the phosphoric acid on the chemically manured plots. It seems probable that this is to be partly accounted for by the supposition that the phosphoric acid contained in the dung, at any rate over a portion of the time, may have been over-estimated. There seems, however, reason to suppose that there has been a greater descent into the subsoil in the case of the plot dunged for fifty years than on the chemically manured plots. On the plot dunged for nine years only we find the estimated accumulation fairly represented in the upper depths—for the most part in the first 9 inches,

Potash Results.

The author has not determined the total potash in the various samples. The Broadbalk soil, like most soils containing much clay, contains a great quantity of potash in the form of silicates, decomposable only by fusion or by treatment with hydrofluoric acid. The quantity of potash, including this, is between 1 and 2 per cent. in the surface soil, and probably more in the subsoil. This means that in the first 9 inches of soil there are probably 15 tons per acre of potash in a dormant form, while the quantity in each succeeding depth is probably greater. Such potash forms a reserve stock for the distant future, and is, no doubt, very gradually rendered available for plant use by the natural processes going on within the soil. But even with this great reserve of total potash, the soil is unable to furnish a sufficient annual supply to the wheat crop under a system of continuous cropping, unless restitution is made in the form of manure.

It is usual in soil analysis to neglect to take into account potash existing in so insoluble a form as to be separable only by means of fusion or treatment with hydrofluoric acid—for such potash is obviously far removed from the range of present utility—and only to take into account such potash as is soluble in hydrochloric acid. It is by this time well recognised, however, that even this solvent extracts, at all events in many cases, far more potash than can be in any sense regarded as of present utility. Unfortunately, this is not the only unsatisfactory aspect of the determination of potash by hydrochloric acid extraction. The quantity of potash extracted varies greatly not only with the strength and quantity of acid used, but also with the duration of the process and with the temperature. Even when like quantities of the same acid and like quantities of soil are taken, and when the evaporation is conducted to dryness in a water-bath, and the residue re-digested with equal quantities of acid, the mere rapidity with which the evaporation to dryness is conducted appears to tangibly affect the quantity of potash extracted from the clay, making concordant duplicate results more or less a matter of chance. It was, however, thought desirable that, for comparison with the citric-acid-soluble figures, such determinations should be made in all of these samples, using in all cases like quantities of acid and soil and operating in as nearly as possible the same manner. The quantity of soil taken for each determination was 10 grammes. The soil was treated with 50 cub. centims. of strong hydrochloric acid, and heated on a water-bath to "dryness," re-digested on the water-bath for one hour with 25 cub. centims. of strong hydrochloric acid, diluted with water, and filtered.

The citric-acid-soluble potash was determined in the solution obtained on treatment of 200 grammes of the soil as described on p. 243, the potash being determined in a quantity of solution representing 50 grammes of soil.

The results are shown in the following table :—

Soils from Broadbalk Wheat Field, Rothamsted.

Samples collected in 1865, 1881, and 1893.

Potash Determinations.

Plot.	Dissolved by strong hydrochloric acid.						Dissolved by 1 per cent. solution of citric acid.					
	K_2O, per cent.			K_2O, lbs. per acre.			K_2O, per cent.			K_2O, lbs. per acre.		
	1865	1881	1893	1865	1881	1893	1865	1881	1893	1865	1881	1893
First 9 inches of soil.												
3	·191	·226	·220	4952	5859	5704	·0040	·0032	·0032	104	83	83
4	—	—	·219	—	—	5678	—	—	·0052	—	—	135
10A	·226	·224	·240	5859	5807	6222	·0040	·0020	·0032	104	52	83
10B	—	·244	·234	—	6326	6067	—	·0032	·0040	—	83	104
11	·228	·243	·197	5911	6300	5107	·0036	·0020	·0032	93	52	83
12	·232	·234	·223	6015	6067	5782	·0060	·0060	·0040	156	156	104
14	·244	·251	·240	6326	6507	6222	·0036	·0044	·0024	93	114	62
13	·269	·290	·273	6974	7519	7078	·0200	·0228	·0188	519	591	487
7	—	—	·262	—	—	6793	—	—	·0232	—	—	602
5	—	—	·279	—	—	7233	—	—	·0308	—	—	799
2B	·273	·259	·285	6767	6206	6652	·0300	·0284	·0384	744	681	896
2A	—	—	·277	—	—	6953	—	—	·0330	—	—	828
Second 9 inches of soil.												
3	·336	·407	·335	8976	10872	8949	·0028	·0044	·0060	75	118	160
4	—	—	·414	—	—	11059	—	—	·0060	—	—	160
10A	·360	·336	·394	9617	8976	10525	·0048	·0024	·0032	128	64	86
10B	—	·374	·359	—	9991	9590	—	·0028	·0052	—	75	139
11	·472	·409	·357	12609	10926	9537	·0052	·0024	·0028	139	64	75
12	·384	·390	·371	10258	10418	9911	·0040	·0028	·0040	107	75	107
14	·491	·403	·404	13116	10765	10792	·0052	·0040	·0048	139	107	128
13	·382	·446	·379	10204	11914	10124	·0120	·0128	·0136	321	342	363
7	—	—	·361	—	—	9643	—	—	·0140	—	—	374
5	—	—	·410	—	—	10952	—	—	·0224	—	—	598
2B	·334	·366	·318	8922	9777	8495	·0140	·0176	·0276	374	470	737
2A	—	—	·398	—	—	10632	—	—	·0168	—	—	449
Third 9 inches of soil.												
3	·459	·466	·495	12813	13008	13818	·0032	·0040	·0072	89	112	201
4	—	—	·507	—	—	14153	—	—	·0044	—	—	123
10A	·511	·475	·533	14265	13260	14879	·0044	·0028	·0048	123	78	134
10B	—	·469	·507	—	13092	14153	—	·0028	·0036	—	78	101
11	·489	·452	·459	13650	12618	12813	·0036	·0028	·0036	101	78	101
12	·456	·505	·488	12729	14097	13623	·0048	·0028	·0036	134	78	101
14	·540	·546	·408	15074	15242	11389	·0040	·0056	·0052	112	156	145
13	·458	·493	·433	12785	13762	12087	·0044	·0032	·0084	123	89	235
7	—	—	·459	—	—	12813	—	—	·0064	—	—	179
5	—	—	·472	—	—	13176	—	—	·0092	—	—	257
2B	·410	·532	·415	11445	14851	11585	·0040	·0052	·0128	112	145	357
2A	—	—	·499	—	—	13930	—	—	·0096	—	—	268

General Comparison of Plots Manured with Potassium Salts (or with Dung) and those not so Manured.

For the purpose of this general comparison it will be sufficient to consider, as in the case of the phosphoric acid results, the 1893 samples—though in this case it will be found to be of interest to consider all the three depths as far as the citric-acid-soluble percentages are concerned. The hydrochloric acid figures, however, for the second and third depths appear to have so little practical significance that we may leave them out of consideration ; the quantity of potash dissolved by the mineral acid in these lower depths being vastly in excess of the potash which, from any point of view, can be regarded as of nearly prospective utility, and its variations being so obviously independent of the manurial treatment and cropping history of the soil as to deprive them of apparent practical significance.

Plot.	Annual manuring for 50 years (with only minor variations during the earlier years).	Percentage of potash in fine dry soil.				Average yield per acre, 1889–1894.	
		Dissolved by hydro-chloric acid.	Dissolved by 1 per cent. citric acid solution.				
		First 9 inches.	First 9 inches.	Second 9 inches.	Third 9 inches.	Wheat.	Straw.
						bush.	cwt.
3	Unmanured continuously . .	·220	·0032	·0060	·0072	12¾	9½
4	Unmanured continuously since 1852	·219	·0052	·0060	·0044	13⅛	9½
10A	Ammonium salts only since 1844	·240	·0032	·0032	·0048	16½	13½
10B	Ammonium salts only since 1850	·234	·0040	·0052	·0036	18	15¼
11	Ammonium salts and super-phosphate	·197	·0032	·0028	·0036	21¾	20½
12	Ammonium salts, superphos-phate, and sodium sulphate (some potassium salts prior to 1852)	·223	·0040	·0040	·0036	29⅛	25⅝
14	Ammonium salts, superphos-phate, and magnesium sul-phate (some potassium salts prior to 1852)	·240	·0024	·0048	·0052	29¼	27⅛
13	Ammonium salts, superphos-phate, and Potassium sulphate	·273	·0188	·0136	·0084	32⅜	31¾
7	Ammonium salts, superphos-phate, and Potassium, sodium and magnesium sulphates . .	·262	·0232	·0140	·0064	34¾	33⅝
5	Superphosphate and Potassium, sodium and magnesium sul-phates (no nitrogen). . . .	·279	·0308	·0224	·0092	14¾	10½
2B	14 tons farmyard manure . .	·285	·0384	·0276	·0128	40⅞	38¾
2A	14 tons farmyard manure (com-mencing in 1884–85) . . .	·277	·0330	·0168	·0096	30¼	28⅜

We have here a series of plots of which some are wholly unmanured, some manured with ammonium salts only, and several with both ammonium salts and phosphates. Of these last, one plot is without alkalies, one receives sodium salts, another magnesium salts, one potassium salts, and another all of these materials. We see that Plot 11 without alkalies, although abundantly supplied with nitrogen and phosphates, has evidently largely exhausted the readily available potash of the soil, by comparing its recent yield of wheat and straw (more especially the latter) with that of the potash Plot 13. We also see that, either in virtue of certain applications of potassium salts forty years or more ago, or possibly in virtue of the solvent action on soil potash of the sodium and magnesium salts applied every year, Plots 12 and 14 are very much more fertile than Plot 11, though distinctly less fertile than Plot 13, which gets an abundance of potassium salts, and still less so than No. 7, which gets all three salts.

The results of the determinations of hydrochloric-acid-soluble potash in the first depths and of the citric-acid-soluble potash in all three depths of the various plots will be seen to possess great interest, and we shall presently have to consider them all in detail.

For the moment, however, we may advantageously condense our table as we did in the case of phosphoric acid, and consider the average results given respectively by the plots manured and unmanured with potash salts and with dung. These are as follows :—

Plots.	Annual manuring for 50 years (with some variations during the earlier years).	Average percentage of potash in fine dry soil.				Average yield per acre, 1889–1894.	
		Dissolved by hydro-chloric acid.	Dissolved by 1 per cent. citric acid solution.				
		1st 9 ins.	1st 9 ins.	2nd 9 ins.	3rd 9 ins.	Grain.	Straw.
3, 4, 10A, 10B, 11, 12, and 14	No potash salts (except odd dressings in early years on 10B, 12, and 14)	·225	·0036	·0046	·0046	Bushels. 20	Cwts. 17$\frac{1}{8}$
13, 7, and 5	All manured annually with dressings including potash salts	·271	·0243	·0167	·0080	27$\frac{1}{4}$	25$\frac{1}{4}$
2B . . .	14 tons farmyard manure yearly	·285	·0384	·0276	·0128	40$\frac{7}{8}$	38$\frac{3}{4}$
2A . . .	14 tons farmyard manure, commencing only in 1884-5	·277	·0330	·0168	·0096	30$\frac{1}{4}$	28$\frac{3}{8}$

The continuous application of potash, whether in the form of potash salts or of dung, has made itself evident in the hydrochloric-acid-soluble potash.   But there is no such difference as, apart from knowledge that the samples are from the same field, would suffice to lead to the conclusion that the soils of the first group were, from a practical point of view, deficient in potash.

Average Ratio of Hydrochloric-acid-soluble Potash in Potash-manured Plots to that in other Plots.

Taking the averages for the first group as unity, we find the following ratios :—

		Ratio of hydrochloric-acid-soluble potash to that in 7 non-potash plots
7 plots.	Without potash for 40 years . .	1·00 : 1
3 ,,	Potash dressed	1·20 : 1
1 plot.	Dung 50 years	1·27 : 1
1 ,,	,, 9 ,, ...	1·23 : 1

Average Ratio of Citric-acid-soluble Potash in Potash-manured Plots to that in other Plots.

A comparison of the citric-acid-soluble potash, however, appears to be much more instructive as to the potash condition of the soils.   The ratios are as follows :—

	Ratio of citric-acid-soluble potash to that in the 7 non-potash plots.		
	1st 9 inches.	2nd 9 inches.	3rd 9 inches.
7 plots. Without potash for 40 years .	1·00 : 1	1·00 : 1	1·00 : 1
3 ,, Potash dressed	6·75 : 1	3·63 : 1	1·74 : 1
1 plot. Dung 50 years	10·67 : 1	6·00 : 1	2·78 : 1
1 ,, ,, 9 ,, ...	9·17 : 1	3·65 : 1	2·09 : 1

These figures are so striking that but little comment on them appears to be necessary.   The chemically manured potash plots show in the first 9 inches nearly seven times as much citric-acid-soluble potash as those left without potash dressings, and in the second 9 inches about three and a half times as much ; while even in the third depth there is nearly twice as much—showing that even in these clayey loams, potash salts do, to an appreciable extent, find their way downwards into the lower subsoil.   The greater portion of the accumulation, however, is (in accordance with the generally accepted views of the chemistry of fairly heavy soils) found to be in the

upper soil, where the potash appears to enter into some kind of chemical combination with the constituents of the clay.

In the continuously dunged soil, where the estimated excess of potash applied has been much greater, we find in the top soil more than ten times as much citric-acid-soluble potash as in the non-potash plots ; in the second 9 inches, six times as much ; and in the third 9 inches, nearly three times as much—while even in the plot dunged for nine years only we find nine times as much in the top soil, three and a half times as much in the second 9 inches, and twice as much in the third. It would seem as though the potash of the dung—possibly in some organic state of combination— descends more easily into the subsoil than do the inorganic potash salts. This point, however, will claim our attention later.

Probable Limit denoting Potash Deficiency in Soil.

In the paper on the Hoos Field barley soils a tentative conclusion was drawn that the percentage of citric-acid-soluble potash in surface soil indicative of potash hunger for cereals would probably lie below 0·005. On considering the results of the wheat-soil analyses and other results obtained in the interim by other workers who have applied the method to other soils known from experience to be responsive to the influence of potassium salts, the author would now be inclined to modify this conclusion by suggesting that when a soil shows as much as 0·01 per cent. of citric-acid-soluble potash, by this process, it may be regarded as *not* demanding any special application of potassium salts.

Plot 3 (Unmanured).

This plot, it will be remembered, has been wholly unmanured throughout the experiments. During the fifty years it has yielded in its crops 761 lbs. of potash. The figures obtained for hydrochloric acid soluble potash in the 1865, 1881, and 1893 samples give no indication of this loss, the quantity found in the 1893 samples being greater than that in the case of the 1865 sample.

The citric acid figures are as follows : —

Potash, per acre, dissolved by 1 per cent. Citric Acid Solution.

	1865. Lb.	1881. Lb.	1893. Lb.
1st 9 inches	104	83	83
2nd ,, ...	75	118	160
3rd ,, ...	89	112	201
27 inches	268	313	444

It will be seen that by 1865, after twenty-two years of cropping without manure, the citric-acid-soluble potash would seem to have been already reduced to a low ebb. In the surface soil it has fallen still lower, but in the second and third depths it would seem to have increased. This decrease to a practically stationary point in the surface soil, accompanied by an increase in the lower depths, was also noticed in the case of phosphoric acid, but the increase, especially in the third depth, is more marked in the case of the potash. It has been already suggested that the phenomenon may be possibly to some extent attributable to the extension of root growth, as the surface soil has become poorer, and to the accumulation of root remains thus formed.

Plots 3 and 4 Compared.

Plot 4, since 1852, has been treated exactly like Plot 3, and by 1893 had been over forty years unmanured. But, as has been already said, it was previously annually dressed with superphosphate and sulphate of ammonia, and in virtue of that treatment has ever since given a slightly better yield than Plot 3 (see comparison as to phosphatic contents on p. 253). It had, in its manured days, no regular supply of potash, but in its first year (fifty years before 1893) it had a dressing of farmyard manure *ashes*, estimated as supplying 235 lbs. per acre of potash. In its crop of fifty years it has yielded 87 lbs. of potash more than Plot 3, but owing to the initial supply referred to, its actual loss in cropping has been 148 lbs. less than that of Plot 3.

This difference is not indicated in the hydrochloric acid potash figures, but it is qualitatively indicated in the surface contents of citric-acid-soluble potash :—

Potash, per acre, dissolved by 1 per cent. Citric Acid Solution.

		Plot 3. Lb.	Plot 4. Lb.
1893.	1st 9 inches . . .	83	135
	2nd ,, . . .	160	160
	3rd ,, . . .	201	123
	27 inches . . .	444	418

Plot 4 contains in the surface soil 52 lbs. per acre more than Plot 3, the 52 lbs. being over one-third of the estimated difference in loss of potash per acre. There is, however, no difference shown in the second 9 inches ; in the third 9 inches Plot 4 is very decidedly poorer. Similar, though less marked, results were found in phosphoric acid. Possibly there has been less root-growth and therefore less accumulation of organic remains in the lower depth, owing to better feeding of the crops.

Plots 3 (*Unmanured*) *and* 10A (*Ammonium Salts only*).

Plot 10A has had ammonium salts every year, without minerals, except in one solitary early year, when it received only 74 lbs. of potash.

Here, again, the hydrochloric acid figures show nothing, but the citric acid figures are of interest.

In the fifty years 10A yielded in its crops 1090 lbs. of potash per acre, against 761 lbs. yielded by 3. Allowing for the 74 lbs. supplied, 10A should be poorer in potash than 3 by 255 lbs. per acre.

The following table shows the citric acid figures for the three sets of samples and the differences found and estimated for the three periods :—

Potash (per Acre) dissolved by 1 per cent. Citric Acid Solution.

Plot.	Found.				More (+) or less (−) than Plot 10A.				Estimated excess of potash in Plot 3, over that in 10A.
	First 9 in.	Second 9 in.	Third 9 in.	27 in.	First 9 in.	Second 9 in.	Third 9 in.	27 in.	

After twenty-two years (1844–65).

	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
10A	104	128	123	355	—	—	—	—	—
3	104	75	89	268	—	− 53	− 34	− 87	+ 142

After thirty-eight years (1844–81).

10A	52	64	78	194	—	—	—	—	—
3	83	118	112	313	+ 31	+ 54	+ 34	+ 119	+ 209

After fifty years (1844–93).

10A	83	86	134	303	—	—	—	—	—
3	83	160	201	444	—	+ 74	+ 67	+ 141	+ 255

In 1865 the surface samples are alike, and 10A is very distinctly richer in the second and third depths. In 1865 10A was showing little sign of potash exhaustion, for in 1866 its crop yielded 29 lbs. of potash per acre, while Plot 3, without nitrogen, gave but 16 lbs. Probably the ammonium salts acted as solvents on the soil potash. By 1881, however, 10A seems to have become appreciably poorer than Plot 3 in all three depths, there being in Plot 3, in the 27 inches, an excess of 119 lbs. per acre, as against 209 lbs. calculated from the crop removals.

By 1893, however, there is a recovery throughout in 10A, possibly owing to the greatly diminished output of crop, to the failure of phosphatic food, and the continued solvent action of ammonium salts, and possibly (for the increase is mainly in the subsoil) partly owing to the effects of deeper root development.

At this time the " available " potash in the surface soil is alike in both plots, but the second and third depths of 3 show together 141 lbs. per acre more than those of 10A, as against a calculated difference of 255 lbs. in the loss due to crop removals during the 50 years.

Plots 10A and 10B.

These plots are alike in their manurial history (ammonium salts every year, without " minerals "), except that while both A and B had a dressing of " minerals " in 1844, Plot B was also dressed with minerals in 1848 and 1850. The effect of these two extra dressings on the yield of Plot B is, as has been already noted, apparent down to the present time.

The extra " minerals " on B included 300 lbs. of potash. During fifty years B, in its crops, has yielded 1205 lbs. of potash, while A has yielded only 1090. Deducting the excess from the supply, Plot B has, however, lost less potash in its crops by 185 lbs. per acre.

Again, the hydrochloric acid results give no indication of this, but the citric acid figures show, even at the end of fifty years, that B is richer than A in soluble potash. The results are as follows :—

Potash per Acre dissolved by 1 per cent. Citric Acid Solution.

	Plot 10A.	Plot 10B.	Excess in 10B over 10A.	
			Found.	Estimated.
	lbs.	lbs.	lbs.	lbs.
1881, first 9 inches . .	52	83	+ 31	——
second 9 inches .	64	75	+ 11	—
third 9 inches .	78	78	—	——
27 inches . .	194	236	+ 42	+ 200
1893, first 9 inches . .	83	104	+ 21	——
second 9 inches .	86	139	+ 53	——
third 9 inches .	134	101	− 33	——
27 inches . .	303	344	+ 41	+ 185

It is notable that in the less starved Plot (10B) there is no increase in the lowest depth as in the case of 10A.

Plots 10A *and* 11. (*Ammonium Salts without and with Phosphates.*)

Both of these plots have been continuously dressed with the same quantity of ammonium salts, but while 10A has (except in one early year) received no minerals, 11 has annually received a dressing of superphosphate.

In fifty years 10A yielded 975 bushels of wheat and 887 cwts. of straw per acre, while 11 yielded 1225 bushels of wheat and 1150 cwts. of straw. 11 has therefore yielded approximately 25 per cent. more wheat and 30 per cent. more straw. For potash supply both crops have annually depended on the natural resources of the soil. The potash contained in the fifty years' produce of 10A has been 1090 lbs., and in that of 11, 1190 lbs. per acre, so that 11 has yielded only about 9 per cent. more potash than 10A. This is evidence—apart from that obtained by comparison with other plots to be presently considered—that the crops of 11 have been relatively, as would be expected, suffering from deficiency of potash, *i.e.*, that the resources of the soil have been inadequate to provide a proper supply. It is therefore of interest to see what evidence the analytical figures show of comparative potash exhaustion in the two soils. This evidence is set forth in the following table :—

Potash (per Acre) dissolved by 1 per cent. Citric Acid Solution.

Plot.	Found.				More (+) or less (−) than Plot 10A.				Estimated deficiency in Plot 11 as compared with Plot 10A.
	First 9 in.	Second 9 in.	Third 9 in.	27 in.	First 9 in.	Second 9 in.	Third 9 in.	27 in.	

After twenty-two years (1844–65).

Plot	First 9 in.	Second 9 in.	Third 9 in.	27 in.	First 9 in.	Second 9 in.	Third 9 in.	27 in.	Estimated deficiency
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
10A	104	128	123	355	—	—	—	—	—
11	93	139	101	333	− 11	+ 11	− 22	− 22	− 90

After thirty-eight years (1844–81).

Plot	First 9 in.	Second 9 in.	Third 9 in.	27 in.	First 9 in.	Second 9 in.	Third 9 in.	27 in.	Estimated deficiency
10A	52	64	78	194	—	—	—	—	—
11	52	64	78	194	—	—	—	—	− 149

After fifty years (1844–93).

Plot	First 9 in.	Second 9 in.	Third 9 in.	27 in.	First 9 in.	Second 9 in.	Third 9 in.	27 in.	Estimated deficiency
10A	83	86	134	3C3	—	—	—	—	—
•11	83	75	101	259	—	− 11	− 33	− 44	− 159

It will be seen that in 1865 a slight deficiency is found in the total 27 inches; that in 1881 the results are the same for both soils; and that in the recently drawn

samples a deficiency is shown of 44 lbs. per acre as against a calculated deficiency of 159 lbs., but that this is mainly found in the lower subsoil. It seems possible that the superphosphate may have helped the crops by dissolving natural potash on Plot 11, and so have prevented a more complete exhaustion. But we must guard against the assumption that all the potash, or any other constituent from the soil, comes solely from the top 27 inches, as the roots go considerably lower.

Plots 3, 10A, and 11 compared.

It is of further interest to compare in the same way both of these plots with Plot 3.

Potash dissolved by 1 per cent. Citric Acid Solution.

Plot.	Found.				More (+) or less (−) than Plot 3.				Estimated deficiency as compared with Plot 3.
	1st 9 inches.	2nd 9 inches.	3rd 9 inches.	Total 27 ins.	1st 9 inches.	2nd 9 inches.	3rd 9 inches.	Total 27 ins.	
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.

Twenty-two years (1844–65).

Plot.	1st	2nd	3rd	Total	1st	2nd	3rd	Total	Estimated
3	104	75	89	268					
10A	104	128	123	355	0	+53	+34	+87	−142
11	93	139	101	333	−11	+64	+12	+65	−232

Thirty-eight years (1844–81).

Plot.	1st	2nd	3rd	Total	1st	2nd	3rd	Total	Estimated
3	83	118	112	313					
10A	52	64	78	194	−31	−54	−34	−119	−209
11	52	64	78	194	−31	−54	−34	−119	−358

Fifty years (1844–93).

Plot.	1st	2nd	3rd	Total	1st	2nd	3rd	Total	Estimated
3	83	160	201	444					
10A	83	86	134	303	0	−74	−67	−141	−255
11	83	75	101	259	0	−85	−100	−185	−414

In the 1865 samples no deficiency is indicated in the existing quantity of readily available potash as reinforced by plant residue accumulation, and possibly by the solvent action of the manures applied; but in the 1881 samples the difference between the unmanured and manured plots has become very marked, and still more so in those of 1893. In this year 55 per cent. of the calculated deficiency of potash per acre on Plot 10A, and about 45 per cent. of that in plot 11, are indicated in the citric-acid-soluble phosphate of the 27 inches of soil, the deficiency in both cases being found in the subsoils.

Plots 11, 12, 13, 14, 7, *and* 5. *Variously Manured. Hydrochloric Acid Results.*

We may now turn to the perhaps more important and practically more interesting series of plots, which have throughout received an abundance of phosphates and (except in one plot) of ammonium salts, but which differ in their treatment as to other saline manures. Here we find that the hydrochloric acid results are of some interest, the accidental variations of analysis which make this determination valueless for showing delicate differences being, to a great extent, overwhelmed by the striking differences exhibited in some of the samples now to be discussed. It is, however, only in the surface soils that the hydrochloric acid figures yield any reliable information, even of a qualitative character, and even then they are of insignificant value besides the citric acid figures. They are, however, set forth in the following table :—

Plots 11, 12, 13, 14, 7, and 5.
Potash per acre dissolved by Hydrochloric Acid from 1st 9 inches of Soil.

Plot and treatment since 1851.	Found.	More (+) or less (−) than Plot 11.	Estimated excess (+) or deficiency (−) per acre as compared with Plot 11.
	Lbs.	Lbs.	Lbs.

After 22 years (1844–1865).

	Found.	More/less	Estimated
11. Nitrogen and phosphates	5911	—	—
12. Ditto and sodium salts (some potash in earlier years)	6015	+ 104	+ 309
14. Ditto and magnesium salts (some potash in earlier years)	6326	+ 415	+ 219
13. Ditto and Potassium salts	6974	+1063	+2021

After 38 years (1844–1881).

	Found.	More/less	Estimated
11. See above	6300	—	—
12. „	6067	− 233	+ 159
14. „	6507	+ 207	+ 54
13. „	7519	+1219	+3222

After 50 years (1844–1893).

	Found.	More/less	Estimated
11. See above	5107	—	—
12. „	5782	+ 675	+ 20
14. „	6222	+1115	− 92
13. „	7078	+1971	+4052
7. Nitrogen, phosphates, potassium, sodium, and magnesium salts	6793	+1686	+3662
5. Ditto, but without nitrogen	7233	+2126	+5242

We find throughout (except in one sample of 1881) a qualitative increase of potash in the soils which have received alkaline salts. In 1893, on two plots — 12 and 14—where the potash was supplied over forty years earlier, and where the quantity supplied has been nearly all removed (as in 12), or more than removed (as in 14), we still find decidedly more hydrochloric-acid-soluble potash than on 11, owing, it may be supposed, to the long continued action of the sodium and magnesium salts applied.

The continuously potash-manured Plot 13 shows in the first 9 inches, soluble in hydrochloric acid, roughly, one-half of the expected accumulation of potash per acre in 1865, three-eighths in 1881, and again nearly one-half in 1893. The difference found between 1881 and 1893 is 752 lbs. per acre against a calculated accumulation of 830 lbs.

Plot 7, with a liberal annual supply of sodium and magnesium salts as well as of potassium salts, has produced persistently larger crops, using more of the potash supplied to it, and retaining per acre, in the fifty years, 390 lbs. less than Plot 13. By hydrochloric acid we find in the surface soil 285 lbs. less, but these close agreements are perhaps to some extent due to coincidence. The citric acid figures are of more interest.

Plots 11, 12, 13, 14, 7, and 5.   Citric Acid Results.

Our starting point for comparison is Plot 11 (ammonium salts and phosphates only). Plot 12, similarly manured, has also for fifty years received sodium salts, but had 588 lbs. of potash in early years. The yield of Plot 12 has averaged nearly 6 bushels of wheat and over 5 cwt. of straw per acre more than that of Plot 11, and in the six years 1889–94 it averaged nearly 8 bushels more grain and 5 cwt. more straw. The larger crops contained in fifty years 553 lbs. more potash, or not quite the whole quantity originally supplied. In 1865 it is estimated that the soil should have been richer in potash than Plot 11 by 309 lbs. per acre; in 1881 by 159 lbs.; and in 1893 by only 20 lbs.

The 1865 sample of Plot 12 (examined, be it always remembered, when nearly thirty years old) shows, in the surface soil, 63 lbs. more citric acid soluble potash than Plot 11; and the 1881 sample shows 105 lbs., with a little in the second depth —making together 116 lbs. excess per acre out of 159 lbs. calculated. By 1893 the calculated accumulation had sunk to 20 lbs. The quantity found by citric acid in the surface soil is 21 lbs., with 32 lbs. in the second depth, making an excess over Plot 11 of 53 lbs. per acre.

This plot (12) is even now much more fertile than Plot 11, although the equivalent of the actual potash added has been nearly used up, and the potash in its produce is still annually far larger than in that of Plot 11. There can be little doubt that the action of the sodium sulphate annually supplied keeps up a considerable annual supply of available potash.

PLOTS 11, 12, 13, 14, 7, and 5.　Potash per acre dissolved by 1 per cent. citric acid solution.

Plot and treatment since 1851.	Found.				More (+) or less (−) than Plot 11.				Estimated excess (+) or deficiency (−) compared with Plot 11.
	1st 9 inches. lbs.	2nd 9 inches. lbs.	3rd 9 inches. lbs.	27 inches. lbs.	1st 9 inches. lbs.	2nd 9 inches. lbs.	3rd 9 inches. lbs.	27 inches. lbs.	lbs.
After 22 years (1844–1865).									
11 nitrogen and phosphates	93	139	101	333	—	—	—	—	—
12 ditto and sodium salts (some potash in earlier years) .	156	107	134	397	+ 63	− 32	+ 33	+ 64	+ 309
14 ditto and magnesium salts (some potash in earlier years)	93	139	112	344	0	0	+ 11	+ 10	+ 219
13 ditto and Potassium salts . . .	519	321	123	963	+ 426	+ 182	+ 22	+ 630	+ 2021
After 38 years (1844–1881).									
11 (see above) . .	52	64	78	194	—	—	—	—	—
12 ,, . .	156	75	78	309	+ 104	+ 11	0	+ 115	+ 159
14 ,, . .	114	107	156	377	+ 62	+ 43	+ 78	+ 183	+ 54
13 ,, . .	591	342	89	1022	+ 539	+ 278	+ 11	+ 828	+ 3222
After 50 years (1844–1893).									
11 (see above) . .	83	75	101	259	—	—	—	—	—
12 ,, . .	104	107	101	312	+ 21	+ 32	0	+ 53	+ 20
14 ,, . .	62	128	145	335	− 21	+ 53	+ 44	+ 76	− 92
13 ,, . .	487	363	235	1087	+ 404	+ 288	+ 134	+ 826	+ 4052
7 nitrogen phosphates, potassium, sodium, and magnesium salts . .	602	374	179	1155	+ 519	+ 299	+ 78	+ 896	+ 3662
5 ditto but no nitrogen	799	598	257	1654	+ 716	+ 523	+ 156	+ 1395	+ 5242

Plot 13, with a full supply of potash, has, in fifty years, yielded about 4 per cent. more grain and about 9 per cent. more straw than Plot 12; but its crops have contained 2410 lbs. of potash per acre as against 1743 lbs. in those of Plot 12.　The

potash-manured crops, therefore, while only from 4 per cent. (grain) to 9 per cent. (straw) larger, have contained nearly 40 per cent. more potash.

Evidence of Action of Sodium and Magnesium Salts as Solvents of Potash.

One might at first sight be somewhat tempted to draw the inference that, in the produce of the sodium sulphate plot (12), soda has partially replaced potash.   In an elaborate study of the vegetative conditions and of the ash constituents of the mixed herbage of grass land, embodied in a recent paper by the late Sir JOHN LAWES and Sir J. HENRY GILBERT ('Phil. Trans.,' Series B, vol. 192, pp. 139–210), we are, however, warned against the temptation to assume that, even in adverse circumstances, soda can *functionally* take the place of potash.   It is pointed out that, in defect of sufficient potash, more of soda or of lime, or of both, will be taken up— probably as carriers of nitric acid—and retained by the plant, but that the herbage will be more leafy and immature than where abundant potash is available.   The free development of carbohydrates functionally demands the presence of an adequate quantity of potash ; and if the plant is stinted in potash neither phosphates nor nitrates, even with the assistance of abundant soda and lime, can enable it to develop to its utmost.   In the last six years of the fifty years now under review the annual produce of Plot 13, with potassium sulphate, has exceeded that of Plot 12 (with sodium sulphate) by $3\frac{1}{4}$ bushels of grain and $6\frac{1}{8}$ cwts. of straw.   Both ripe grain and straw consist mainly of carbohydrates, and the excess virtually indicates the greater carbohydrate elaborative power conferred on the wheat plant by supplying it freely with potassium salts, and the inability of sodium salts to functionally replace them.

But the output of potash from Plot 12 in quite recent years is so much greater than from Plot 11 without either potash or soda that there can be little doubt of the practical action of the sodium salts as solvents of soil potash.

Plot 14 is similar in every way in its history to Plot 12, except that it has been annually dressed with 280 lbs. of magnesium sulphate instead of $366\frac{1}{2}$ lbs. of sodium sulphate.   Its yield, though less than that of Plot 13, has been, on the average of fifty years, slightly better than that of Plot 12, over half a bushel of wheat and nearly 1 cwt. of straw being the annual advantage.   In later years the inferiority to Plot 13 has become more marked, but the superiority to 12 is still distinct, especially in the yield of straw.   While receiving slightly less potash in its early dressings than Plot 12, Plot 14 has given in crops nearly 100 lbs. more potash in fifty years.

The soil samples taken of this plot in 1865, in citric-acid-soluble potash, indicate a less accumulation than those of Plot 12.   But in the 1881 samples there is a considerable increase in citric-acid-soluble potash.   In that year 54 lbs. more potash per acre should be expected in this plot than in Plot 11.   Actually we find, soluble in citric acid, 62 lbs. more in the surface soil, 43 lbs. in the second 9 inches, and 78 lbs. in the third 9 inches—making 183 lbs. per acre more than on Plot 11, as against 54 lbs. expected accumulation.

Passing on to the 1893 samples, when there should, by calculation, be now a deficit of 92 lbs. of potash per acre, compared with Plot 11, we begin to lose some of our accumulation. The surface soil yields much less citric-acid-soluble potash than in 1881, but the second and third depths maintain their superiority, leaving (compared with Plot 11) a balance to the good of 76 lbs. per acre of easily soluble potash in the 27 inches of soil, as against a calculated deficiency, owing to cropping, of 92 lbs. From these facts, as well as from the higher output of potash from this soil, there seems to be little doubt that the magnesium sulphate, like the sodium sulphate, has acted as a potash solvent, but to an appreciably greater extent, especially in the subsoil.

We now pass on to Plot 13, which has received, in addition to ammonium salts and superphosphate, a liberal annual dressing of potash far in excess of the demands of the crop. The excess of supply of potash per acre over the output of potash in the crops should leave the plot richer than Plot 11 to the extent of 2021 lbs. per acre in 1865, of 3222 lbs. per acre in 1881, and 4052 lbs. per acre in 1893. We find soluble in citric acid solution, in the 27 inches of soil, compared with Plot 11, an excess of 629 lbs. per acre in 1865, of 828 lbs. in 1881, and of 827 lbs. in 1893. At the end of the two earlier periods this excess is nearly all found in the first and second 9 inches, but in 1893 there is found a large increase in the third 9 inches also, indicating a descent of potassium salts. But the citric-acid-soluble accumulation even in the whole 27 inches, though so great, is, roughly, only 30 per cent. of the expected accumulation in 1865, only 25 per cent. in 1881, and 20 per cent. in 1893. Either, therefore, much of the potash has been washed down to lower depths still, or it has "reverted" into some form of combination with the bases of the soil in which its fails to be dissolved by weak citric acid solution.

Probably, as we shall see presently, much of the deficiency is to be accounted for by descent.

Plot 7 is manured like Plot 14, but has, in addition to potassium salts, received also an annual dressing of sodium and magnesium salts. Only the 1893 samples of soil have been investigated. This plot has, on the average, yielded 1½ bushels more wheat and 1⅝ cwts. more straw per acre than Plot 13; while in the last six years (1889-94) it gave 2⅔ bushels more of wheat and 1⅞ cwts. more straw per acre. Its larger yield of crops has entailed a distinctly larger output of potash, so that the estimated excess in the soil (3662 lbs. more than Plot 11) is 390 lbs. less than on Plot 13. Citric acid dissolves, however, from this soil, 115 lbs. more than from Plot 13 in the surface soil, and 11 lbs. more in the second 9 inches, but 56 lbs. less in the third 9 inches, leaving a balance of 70 lbs. in favour of Plot 7 in the whole 27 inches. On the whole and mainly in the surface soil it would seem that the magnesium and sodium salts have effected the retention of considerably more of the potash in an easily soluble condition.

Plot 5 is a duplicate of Plot 7 with, however, the very important exception that it

has received no nitrogenous manure whatever.   It yields but meagre crops—better, it is true, than those of the wholly unmanured soil—even now after fifty years.   But it has given less than half the wheat of Plot 7 and about three-eighths of the straw of that plot, while in recent years it has given less than one-third of the straw.   Its estimated excess of potash, as compared with Plot 11, is 5242 lbs., or 1580 lbs. more than Plot 7.   The surface soil is richer in potash than that of Plot 7 by 203 lbs., the second 9 inches by 225 lbs., and the third 9 inches by 78 lbs., making, in the 27 inches, just 500 lbs. per acre, or nearly one-third of the estimated difference.

The Dunged Plots (2A and 2B).

We have yet to consider the two farmyard manure plots, 2B and 2A, the former of which has continuously received throughout the experiments 14 tons of dung per acre per annum, while the latter has been similarly dressed since 1884 only, having been previously unmanured.

For a discussion of this plot the reader is referred back to p. 264 where the phosphoric acid results are referred to.

Plot 2B may be conveniently taken first.   The following table is self-explanatory :—

Plot 2B (Dung for Fifty Years).

	After twenty-two years (1844–1865).	After thirty-eight years (1844–1881).	After fifty years (1844–1893).
	lbs. per acre.	lbs. per acre.	lbs. per acre.
Estimated excess of potash per acre over Plot 3	4532	7773	10043
Excess of potash over that in Plot 3 found soluble in strong hydrochloric acid in first 9 inches . .	1815	347	948
Excess of potash over that in Plot 3 found soluble in 1 per cent. solution of citric acid :—			
First 9 inches	640	598	813
Second 9 inches	299	352	577
Third 9 inches	23	33	156
27 inches	962	983	1546

The hydrochloric acid figures show qualitatively an excess in each case, but it is of no quantitative significance.   In the lower depths the corresponding figures have no significance whatever—being widely variable.   The citric acid results show a progressive increase, but the 1881 samples do not occupy, as to their results, the intermediate position between the other two sets that would be expected.

Only about 21 per cent. of the expected accumulation is found in the three depths

of 1865, in a citric-acid-soluble state, only about 13 per cent. in those of 1881 and less than 16 per cent. in those of 1893.

The potash in the dung is estimated by Sir HENRY GILBERT at 0·75 per cent. The difficulty of forming an accurate estimate of the average constituents of so variable a substance as dung has been already discussed under phosphoric acid (see p. 264). The author is inclined to think that the average richness of the dung in potash may have been over-estimated. On the estimate adopted (0·75 per cent.) the potash supplied to the soil in fifty years amounts to no less than 11,760 lbs. An average error of only 0·1 per cent. in the estimate would therefore amount to 1570 lbs. per acre, and an error of 0·25 to 3920 lbs. per acre. But even after making liberal allowance for this, there is a large proportion of potash not accounted for in the citric-acid-soluble contents of the soil, which must either have remained in (or reverted into) an insoluble condition, or have descended still lower into the subsoil. Possibly both suppositions are true, for there is—certainly in 1893—clear evidence of excess as far as the third depth. It has already been suggested that earth-worms may possibly be responsible for the mechanical transfer of dung to the lower subsoil.

In the case of Plot 2A—dunged for only nine years previously to 1893—the figures work out as in the following table :—

Plot 2A (Dung for Nine Years) (Unmanured for preceding Forty-one Years) (1893).

	lbs. per acre.
Estimated excess of potash per acre over Plot 3	1892
Excess of potash over Plot 3 found soluble in strong hydrochloric acid in first 9 inches	1249
Excess of potash over Plot 3 found soluble in 1 per cent. citric acid solution :—	
First 9 inches	745
Second 9 inches	289
Third 9 inches	67
27 inches	1101

Here the figures found by analysis are much more in accord with estimate, and it is obvious that whatever error there may be in the potash estimate for the dung has only been multiplied nine-fold instead of fifty-fold; and it is further possible that the estimate adopted may be more accurate for the dung recently used than for that of earlier years. There seems, however, to be evidence here again that the potash of the dung travels downwards with considerable facility, for though the dunging has only been continued for nine years, there is a great increase in the soluble potash of the second 9 inches, and a considerable increase in that found even in the third 9 inches. Altogether the citric-acid-soluble potash found in the 27 inches accounts for nearly two-thirds of the estimated excess in the soil, as compared with Plot 3.

POTASH IN DRAINAGE WATERS.

(*Analyses by the late Dr.* A. VOELCKER) : *Loss of Potash by drainage generally slight, but very appreciable on dunged plot and on plot manured with Potash in absence of Nitrogenous Manure.*

Under the section on phosphoric acid reference was made (p. 267) to the results of the analyses of drainage waters of Broadbalk Field made in 1867, 1868, and 1869, by the late Dr. A. VOELCKER. Samples taken in May, 1867, January and April, 1868, and December, 1869, yielded the following average quantities of potash per million :—

	Average quantity of potash in drainage waters. Parts per million.
Plots 3 and 4 (unmanured)	1·7
Plot 10 (ammonium salts only)	1·9
,, 11 (ammonium salts and superphosphate) . . .	1·0
,, 12 (ammonium salts, superphosphate, and sodium sulphate)	2·7
,, 14 (ammonium salts, superphosphate, and magnesium sulphate)	1·0
,, 13 (ammonium salts, superphosphate, and potassium sulphate)	3·3
,, 7 (ammonium salts and full minerals)	2·9
,, 5 (full minerals without nitrogen)	5·4
,, 2 (farmyard manure)	5·4

These results, although the samples examined were few in number, accord on the whole remarkably with what might be expected, in the light of the foregoing discussion. Thus the potash in the drainage water is less on Plot 11—supplied with phosphates and nitrogen, but no potash—than on the unmanured Plots 3 and 4, or on Plot 10, which received only ammonium salts; the utilisation by crops of the available potash being, of course, greater on Plot 11 in presence of abundance of both phosphates and nitrogen. Plot 12, supplied in its earlier history with potash, and in virtue of this (and probably of the solvent action of the sodium salts) showing, in the 1865 soil samples, more citric-acid-soluble potash than Plot 11, also yields more potash in its drainage water; and it also yields more than Plot 14 (magnesium salts), also in accordance with the citric acid results. Plot 13, well supplied with potash, shows decidedly more potash in its drainage water than Plot 7, also liberally supplied with potash, but getting also other salts, and giving in consequence a greater crop, and utilising somewhat more potash; while Plot 5, getting a full supply of minerals without nitrogen, yields much more potash in its drainage (as much as the dunged

plot, which receives the greatest quantity of potash). The average quantities are, it is true, in no case great, varying from 1 part of potash per million parts of water on Plots 11 and 14 to 5·4 parts per million on Plots 5 and 2.

Assuming an average annual percolation of 10 inches of rain water into the drain-pipes or into the subsoil below the depth of 27 inches, these quantities would represent as little as $2\frac{1}{2}$ lbs. of potash per acre per annum from Plots 11 and 14, and as much as $12\frac{1}{2}$ lbs. per acre from Plot 5 (full mineral dressing without nitrogen), and from Plot 2 (continuously dunged). The difference between these two extremes would amount to 500 lbs. in fifty years; but it seems probable that as the quantity of potassium salts has annually accumulated in the soil, the quantity of potash in the drainage waters will have become greater in later years on the potash-manured plots and on the continuously dunged plot.

Dr. A. VOELCKER's drainage water analyses, therefore, may be regarded as yielding, even as long ago as 1867–69, evidence of appreciable descent on the plot on which the application of potassium salts had been excessive, and where their utilisation had been least, owing to absence of nitrogenous manure : and also on the plot on which the heavy dressing of farmyard manure had been continuously applied.

The analytical results of the subsoils of these plots down to a depth of 27 inches show a much larger quantity of citric-acid-soluble potash than do any of the other plots, and this seems to accord with the indications of the descent of some potash to even a lower depth in the drainage water.

SUMMARY AND GENERAL CONCLUSIONS AS TO POTASH.

The hydrochloric acid solubility of potash is, as in the case of the barley soils, found to be practically useless as a gauge of potash fertility, especially in soils containing an abundance of total potash in mineral combination as silicates, &c. No concordant results are obtainable except by working under the strictest arbitrary conditions, and the results, when concordantly obtained, have little meaning, apart from an independent knowledge of the history of the soil. With this knowledge the results are interesting, but in its absence are of little use even as a vague index of potash fertility, except in extreme cases.

The results obtained by the use of dilute citric acid as a solvent are very strikingly instructive and consistent. They show that the largest accumulation of manurial potash, whether applied in the form of dung or of potassium salts, is in the surface soil, but that a very large proportion is also found in the second 9 inches, and even in the third 9 inches. The accumulation in the second and third 9 inches is most evident in the cases of the dunged plots and of the plot which, in addition to potassium salts, has received superphosphate and sodium and magnesium sulphates, without nitrogen. Both sodium and magnesium salts have exercised a distinct influence in increasing the proportion of citric-acid-soluble potash, in all depths, on

the plots to which no potassium salts have been applied for over forty years. These plots still maintain a higher yield of potash in their crops than does the plot manured with superphosphate and ammonium salts only, though the equivalent of the potash originally added has been more than exhausted in one case, and nearly so in the other. Furthermore, sodium and magnesium salts, used in conjunction with potassium salts, have caused a much larger retention of potash in a citric-acid-soluble condition than when potassium sulphate has been used without them, although the potash taken up by the crops has been greater than in the latter case.

It would seem on the whole probable that when a soil, in the surface depth, contains as much as 0·01 per cent. of citric-acid-soluble potash the special application of potassium salts, at any rate as far as cereals are concerned, is not needed.

It has usually been considered that potash is pretty firmly retained in the surface soil on land containing a fair proportion of clay. That this is the case, as compared with sodium salts, has often been shown, and, apart from earlier investigations, was markedly brought out in the Broadbalk drainage water analyses made by the late Dr. A. VOELCKER, which showed that sodium salts pass into the drainage water with comparative freedom, while potash was found in only comparatively small quantities. But, as we have seen, even the water analyses referred to did show a distinct loss of potash in drainage in certain cases, and it is evident from the results of the surface soil and subsoil analyses now discussed that, though, relatively to sodium salts, potassium salts readily become " fixed " in soils, often probably passing partially into a very stable insoluble form, they are nevertheless far more " migratory " than phosphoric acid.